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Physics. — *"On the Cohesive Forces of Liquids"*. By A. TH. VAN URK. (Communicated by Prof. H. A. LORENTZ).

(Communicated at the meeting of March 28, 1925).

§ 1. *Introduction.*

In 1805 shortly after each other appeared the theories of YOUNG[1]) and LAPLACE[2]) on the cohesion of liquids, of which the latter has held its grounds up to now, whereas YOUNG's theory is almost forgotten.

In VAN DER WAALS's well-known thesis for the doctorate: „On the Continuity of the Gaseous and the Liquid State" we find YOUNG's name not even mentioned in the discussion of LAPLACE's theory, so that probably VAN DER WAALS did not know YOUNG's work. Yet YOUNG already gives an estimation of the internal pressure and of the distance of the elementary liquid atoms, and besides of the range over which the attractive force acts. It appears already here that YOUNG finds these two distances of the same order of magnitude. The same thing is also stated by VAN DER WAALS in the above-mentioned thesis for the doctorate.

An excellent survey of YOUNG's and LAPLACE's theories (the latter given according to MAXWELL) is to be found in RAYLEIGH, Collected Papers, Vol III, p. 396. It is unnecessary to repeat his calculations here; we will only mention some results:

$$K_0 = \frac{2\pi}{3}\int_0^\infty z^3\,\varphi(z)\,dz \qquad T_0 = \frac{\pi}{8}\int_0^\infty z^4\,\varphi(z)\,dz.$$

In this K_0 is the internal pressure, and T_0 the surface tension z representing the distances of the molecules; $\varphi(z)$ is a force, a function of z, which is insensible for all sensible values of z, but which becomes sensible and even enormously great, when z is exceedingly small.

As the simplest example of such a force RAYLEIGH gives $\varphi(z) = e^{-\beta z}$. This yields for the relation of T_0 and K_0: $T_0 = \frac{3}{4}\frac{1}{\beta}K_0$. $\left(\text{The range of the force is of the order of magnitude } \frac{1}{\beta}\right)$.

As a second example RAYLEIGH takes $\varphi(z) = z^n$, and finds that for any value of n, whatever it may be, the internal pressure becomes infinite.

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[1]) YOUNG. On the cohesion of fluids. Phil. Trans. 1805. Vol. II, p. 657.

[2]) LAPLACE, Méc. Cél. Tome IV, p. 399.

The cause of this lies in the fact that Rayleigh takes zero for the lower limit of integration, which is not allowed for other than point-molecules. Young himself gives $T_0 = \frac{1}{3} a\ K_0 \left(a = \frac{1}{\beta} \right)$ as relation between T_0 and K_0. Rayleigh, however, as result of the calculation according to Young's supposition: i.e. an attractive force constant for the small distance over which it acts balanced by a repulsive force in inverse ratio to the distance, $T_0 = \frac{3}{20} a K_0$.

Rayleigh says about this difference in result: „The discrepancy seems to depend upon Young having treated the attractive force as operative in one direction only". I have not succeeded in seeing this part of Young's work, hence I have not been able to form an opinion on this point.

Further van der Waals gives a theory on surface tension [1]), in which he assumes $-\Pi(f) = \frac{Ae^{-z/\lambda}}{\lambda} \left(\lambda = a = \frac{1}{\beta} \right)$ as potential of the attractive forces. This assumption yields $T_0 = \frac{1}{2} \lambda K_0$. The coefficient $1/2$ is in agreement with what Stefan already expected for the ratio between the work required to bring a molecule at the surface and that required to bring a molecule quite outside the reach of the liquid fields of force when van der Waals's equation of state is valid. [2])

Hence it appears from the results given that with a theory in which the forces vary continuously with the distance and reach many molecules far, widely divergent results are possible, dependent on the force function assumed.

Now it has, however, already appeared from van der Waals's and Young's estimations that the attractive forces operate over distances comparable with the diameter of the molecules, and in „Bemerkung zu dem Gesetz von Eötvös" [3]) also Einstein arrives by a theoretical way at the result that the attractive forces act only between molecules lying immediately side by side.

The direct experimental proof has finally been furnished by Langmuir's researches on mono-molecular liquid films [4]). They form the conclusion of a long series of researches starting with Miss Pockels and Rayleigh. They seem to have been prompted by a remark of Maxwell in the Scientific Papers Vol. II p. 549, viz:

"The phenomenon of very thin liquid films deserve the most careful study, for it is in this way that we are most likely to obtain evidence by which we may test the theories of the molecular structure of liquids".

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[1]) v. d. Waals—Kohnstamm 1er Teil p. 208.

[2]) Wiedem. Ann. Bd. 29. p. 655, 1886. Compare also Kuenen: Die Eigenschaften der Gase Kap. 14. p. 380, et seq..

[3]) Ann. der Physik 1911. Bd. 34.

[4]) Journ. of the Am. Chem. Soc. Vol. 38. Nov. and Vol. 39. Sept.

It seems desirable to me to calculate the internal pressure and the surface tension with such forces, the more so where it is possible to test the results by experimental data. So far it has been only rarely tried to compare the relations between T_0 and K_0 with the data. I am only acquainted with the comparison by EINSTEIN (loc. cit.) for benzene and mercury, and VAN LAAR's computations in the Chemisch Weekblad of 1918 and 1919. He tries to show via VAN DER WAALS'S a that RAYLEIGH's recorded result $^3/_{20}$ conforms about to reality for so-called normal (i. e. non-associating substances. In what follows a relation will be drawn up for *simple* gases and examined for them, in contrast with LANGMUIR, who has always worked with very complicated organic substances.

§ 2. *Calculation of the formulae.*

Following LANGMUIR we shall suppose that the forces are specific: i. e. entirely determined by the molecule from which they start; operating in definite directions;

that their range is restricted to the molecules lying nearest;

that the number of molecules that can enter into interaction with a definite molecule is entirely controlled by the number of directions of force issuing from the molecules.

We now get the following image of a liquid:

Every molecule has a same number of directions of force along which the forces act through which the molecules are connected with each other, and which we shall call rods in what follows. If we now suppose the liquid without heat motion, hence cooled down to the absolute zero point, but remaining liquid and not crystallized (i. e. without particular structure), we can calculate T_0 and K_0 accurately; at least if all the rods have the same length and are equally strong. In this case we shall assume the substance in the solid state to be regular. In the calculation we shall make use of the property that internal pressure and internal heat of evaporation per ccm. are represented by the same number. (See RAYLEIGH, loc. cit. p. 421).

If we now take a cube of liquid of 1 ccm., containing N molecules, and if every molecule possesses k rods, the total number of rods per unit volume is $\frac{Nk}{2}$.

If we call the work required to break one rod, s, the total work to break all the rods, hence the internal heat of evaporation is $\frac{Nks}{2}$.

To calculate the surface tension we may proceed as follows: we take a plane, parallel to the plane of the cube, and calculate how many rods intersect this plane. The work required to break the cube according to this plane is equal to twice the surface tension. The rods will now have all possible orientations in the liquid. The number of rods that form an angle between θ and $\theta + d\theta$ with the normal to the plane considered is $\frac{Nk}{2} \cdot \frac{2\pi \sin \theta \, d\theta}{4\pi}$ per unit of volume. Let all the rods have the same length l, rods forming an angle θ with the normal, will still just intersect the plane, if they lie in the parallelepiped that adjoins the plane and has a height equal to $l \cos \theta$. This holds for both sides of the plane, and as θ can vary from 0 to $\frac{\pi}{2}$ the total number of rods intersecting the plane is:

$$\int_0^{\pi/2} \frac{Nk}{2} \cdot \frac{2\pi \sin \theta \, d\theta}{4\pi} \, . \, l \cos \theta \, . \, 2 \, . = \frac{Nkl}{2} \int_0^{\pi/2} \sin \theta \cos \theta \, d\theta = \frac{Nkl}{4} \sin^2 \theta \, \Big|_0^{\pi/2} = \frac{Nkl}{4}$$

Hence the surface tension is $\frac{Nk\,ls}{8}$.

We find for the relation of T_0 and K_0:

$$\frac{2\,Nk\,ls}{8\,Nks} = \frac{l}{4} \text{ hence } T_0 = \frac{1}{4}\, l\, K_0 \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

For the numerical calculation it is convenient to transform this formula somewhat. Multiply left and right by $\left(\frac{M}{d} \cdot \frac{1}{N}\right)^{2/3}$, then we may write:

$$\left(\frac{M}{d} \cdot \frac{1}{N}\right)^{2/3} . \; T_0 = \frac{1}{4} \cdot \left(\frac{M}{d} \cdot \frac{1}{N}\right) K_0 \, . \, \frac{l}{\left(\frac{M}{d} \cdot \frac{1}{N}\right)} \quad . \; . \; . \; . \quad (2)$$

Now $\frac{M}{d}$ is the number of ccm. per gr. mol., hence $\frac{M}{d} \cdot \frac{1}{N}$ the vol. per molecule in ccm., and $\frac{M}{d} \cdot \frac{1}{N} \cdot K_0$ is the work for the vol. of a molecule, hence required to detach a molecule. $\left(\frac{M}{d}\right)^{2/3} T_0$ is the molecular surface tension.

We must finally make some conclusion about the length of the rods and the number of molecules in a surface of the cube that contains a gramme-molecule. In what follows $N^{2/3}$ has been assumed for the required number, and $\left(\frac{M}{d} \cdot \frac{1}{N}\right)^{1/3}$ for the length, i. e. the side of a cube occupying the same volume as is available for a molecule. If it is, however, assumed that the molecules fill the volumes as spheres packed as closely together as possible, the length would have to be $l_1 = 1{,}12\, l$. Instead of $\frac{1}{4}$ the constant of the formula would then have become 0,28.

Recapitulating we see that the lefthand member of equation (2) represents the mean surface tension per molecule σ_0, and the righthand member without the coefficient $\frac{1}{4}$ the mean internal heat of evaporation per molecule L_0, both at the absolute zero. Hence formula (2) becomes:

$$\sigma_0 = \frac{1}{4} L_0 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

§ 3. *Testing by the data.*

For the surface tension there are available BALY and DONNAN's measurements on hydrogen, nitrogen, and argon [1]), and those of KAMERLINGH ONNES and KUYPERS on hydrogen [2]).

On the heat of evaporation of the same substances publications have appeared by MATHIAS, CROMMELIN, and KAMERLINGH ONNES [3]). To obtain the σ_0 from formula (3) it is sufficient to put $T=0$ in the formula for the molecular surface tension of BALY and DONNAN, and divide by $N^{2/3}$. The internal heat of evaporation is obtained by diminishing the values of the heat of evaporation with the external work; the values found thus were plotted on a large scale, and then extrapolated linearly to $T=0$. For greater certainty in this graphical representation also the values of the heat of evaporation itself were plotted, to see if the heat of evaporation goes to the same point on extrapolation.

We now multiply these values by the molecular weight and the mechanical equivalent of heat, and divide by N. We get the internal heat of evaporation in ergs per molecule at $T=0$, hence the L_0 from the righthand member of equation (3).

Of the four substances given hydrogen is regular, probably triakis- or hexakis-octahedral, argon and nitrogen regular at the melting-point, and oxygen hexagonal at the melting-point according to visual observations by W. WAHL [4]). This has since been confirmed by Röntgenograms at Leiden and Berlin.

We shall give the data below.

Constants used:

N (number of mol. per gramme-mol.) $6.062.10^{23}$.

Mech. equivalent of heat $4.189.10^{7}$.

Molecular weights: hydrogen 2.016, argon 39.9, nitrogen 28.00 and oxygen 36.00.

Molecular surface tensions:

Hydrogen: $\sigma = 1.294\,(34.49 - T)$ [5]).

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[1]) Journ. of the Chem. Soc. **81**, pg. 907. 1902.

[2]) Leiden Comm. N⁰. 142*d*.

[3]) Leiden Comm. N⁰. 162.

[4]) W. WAHL. Zeits. für phys. chem. Bd. **84**. 1913 p. 101.

[5]) This formula has been calculated from KAMERLINGH ONNES' and KUYPERS' observations.

Argon: $\sigma = 2.02\ (145.44 - T)$.
Nitrogen: $\sigma = 2.002\ (124.29 - T)$.
Oxygen: $\sigma = 1.917\ (153.77 - T)$.

Heats of evaporation:

Hydrogen				Nitrogen			
T	L (gr. cal.)	W	L_i	T	L (gr. cal.)	W	L_i
32.52	35.40	8.11	27.3	125.01	9.17	2.04	7.13
31.26	58.14	12.26	45.9	124.48	11.40	2.33	9.07
30.06	71.44	14.26	57.2	123.34	15.03	2.82	12.21
28.79	81.45	16.62	64.8	119.44	22.96	3.86	19.10
27.36	89.62	17.69	71.9	111.89	31.73	5.07	26.66
25.30	97.58	18.63	78.9	99.36	39.63	5.70	33.93
23.20	102.6	18.4	84.2	90.58	43.09	5.83	37.26
20.41	106.2	17.7	88.5	78.00	47.06	5.32	41.74
19.85	106.6	17.5	89.1	73.06	48.64	5.08	43.56
19.33	107.0	17.5	89.5	67.64	50.52	4.72	45.80
17.90	107.8	16.6	91.2	64.73	51.64	4.41	47.23
17.10	108.1	16.0	92.1	0	71.5	0	71.5
16.34	108.5	15.0	93.5				
15.86	108.7	14.8	94.9				
14.82	109.3	13.7	95.6				
0	112.	0	112.				

After having calculated the L_0 and σ_0 from the extrapolation values thus obtained, we get the following survey, (To give some idea of the order of magnitude the kinetic energy per degree of freedom at the critical temperature (kT_k) and the dissociation energy [1]) per molecule have been added).

Let us start with the relation of σ_0 and L_0. For nitrogen and argon this is within the margin of errors $\frac{1}{4}$, for oxygen 0.267. It seems, therefore, that though oxygen is hexagonal, the strength of the bonds in the

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[1]) J. J. VAN LAAR. Die Zustandsgleichung p. 215.

Argon				Oxygen			
T	L (gr. cal.)	W	L_i	T	L (gr. cal.)	W	L_i
147.92	10.50	2.19	8.31	152.7	11.23	2.91	8.32
141.55	18.53	3.28	15.25	149.8	18.62	3.50	15.12
137.58	21.74	3.32	18.42	143.2	28.15	4.85	23.30
132.89	24.73	3.88	20.85	132.9	36.72	5.46	31.26
122.33	29.62	4.55	25.07	118.6	43.54	5.61	37.93
111.86	33.02	4.66	28.36	91.1	50.29	5.04	45.25
97.70	36.50	4.45	32.05	62.7	56.44	3.45	52.99
89.94	38.15	3.97	34.18	0	70.0	0	70.0
0	59.0	0	59.0				

	$L_0 \cdot 10^{14}$	$\sigma_0 \cdot 10^{14}$	$kT_k \cdot 10^{14}$	D.En. . 10^{14}
H_2	1.55	0.62	0.456	600
N_2	13.9	3.47	1.729	1000
A	16.3	4.10	2.067	
O_2	15.5	4.12	2.116	1100

different directions does not differ much. In hydrogen, though it is regular, the ratio is $\frac{\sigma_0}{L_0} = 0{,}40$.

In conformity with a remark by EINSTEIN (loc. cit.) that in substances with very small molecules the radius of the molecular sphere of action would be greater than three times the radius of the molecule, and taking into consideration the poly-planed crystalline structure, we might try to account for this by assuming that every hydrogen molecule has two kinds of rods. We must then distinguish two groups of rods, the first with number k_1, length l_1, and strength s_1, the second with k_2, l_2, s_2.

We may make the following plausible supposition: $l_2 = 2l$, and $k_2 = 2^2 k_1$, because probably $\frac{k_2}{k_1} = \frac{4\pi l_2^2}{4\pi l_1^2} = \frac{l_2^2}{l_1^2}$ will hold.

Then the formulae become:

$$K_0 = \frac{N}{2}(k_1 s_1 + k_2 s_2) \qquad T_0 = \frac{N}{8}(k_1 l_1 s_1 + k_2 l_2 s_2)$$

$$K_0 = \frac{N}{2} k_1 (s_1 + 2^2 s_2) \qquad T_0 = \frac{N}{8} k_1 l_1 (s_1 + 2^3 s_2)$$

$$\frac{T_0}{K_0} = \frac{l_1}{4} \frac{s_1 + 2^3 s_2}{s_1 + 2^2 s_2}.$$

Taking $\frac{\sigma_0}{L_0} = 0.40$ (hydrogen), we find from the formula:

$$\frac{\sigma_0}{L_0} = \frac{1}{4} + \frac{s_2}{s_1 + 2^2 s_2} \text{ or } s_2 = 0.37\, s_1.$$

When we extend this procedure to n kinds of rods, we get the following: $l_n = n l_1$ and $k_n = n^2 k_1$.

$$\frac{T_0}{K_0} = \frac{l_1}{4} \frac{s_1 + 2^3 s_2 + 3^3 s_3 + \ldots n^3 s_n}{s_1 + 2^2 s_2 + 3^2 s_3 + \ldots n^2 s_n}$$

and in this a definite course of s gives a definite ratio of $\frac{T_0}{K_0}$, hence also of $\frac{\sigma_0}{L_0}$. On transition of n to infinite we should then get back the integrals of the beginning.

I think it, however, necessary to point out that there is some doubt about the correctness of the data for hydrogen. SIMON and LANGE believe they have observed a maximum in the heat of evaporation [1]) and the formula for σ in hydrogen departs from the formulae of the three other gases. In the three latter gases the temperature at which $\sigma = 0$, is smaller than the critical, whereas it is greater in hydrogen.

As regards the order of magnitude we might expect according to the formula of EÖTVÖS, that kT_k should be of the same order. It is, however, surprising in nitrogen and argon that L_0 and σ_0 are a whole number of times kT_k.

In these simple substances the energies of dissociation are many times greater than the heats of evaporation, the ratio for water of 0° C. on the contrary being about 6 to 1.

The method of comparing σ_0 and L_0 followed here cannot be applied for less simple substances. Not only does the extrapolation become more and more doubtful in consequence of the rise of the melting-point, but besides it is necessary to know something about the position of the molecule in the surface, this being of great influence on the number of molecules per cm^2. In an imaginary plane intersecting the liquid, not the same number of molecules will be present as in a cm^2 of the surface. Nor will the reasoning be valid for not regularly crystallizing substances, because the molecules will assume a definite orientation in the surface not only dependent on the form, but also on the difference of force in the different directions.

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[1]) Zeitsch. für Phys. Bd. **15.** (1923) p. 312. The two values through which they conclude to a maximum, differ only about 1 %.

[2]) Leiden Comm. phys. lab, Suppl. N⁰. 23. and Enc. der Math. Wiss. Art. V 10 note 528.

At the conclusion of this article it is a privilege to me to express my indebtedness to Prof. Dr. H. A. LORENTZ for the readiness with which he always put his time at my disposal to discuss these questions with me. To him, and to Prof. Dr. W. H. KEESOM, to whom I also express my thanks here, I owe many a valuable suggestion.

Mathematics. — *“The Complete System of Invariants of Two Covariant Antisymmetrical Tensors of the Second Order and an arbitrary Number of Vectors”*. By G. F. C. GRISS. (Communicated by Prof. R. WEITZENBÖCK).

(Communicated at the meeting of March 28, 1925).

1. We start from a system of 2 antisymmetrical tensors p_{ik} and q_{ik} and r covariant vectors ${}_1a_i, \ldots, {}_ra_i \; (i, k = 1, \ldots, n)$ and we shall determine its complete system of invariants by the aid of the symbolical method [1]).

We write symbolically

$$p_{ik} = p_i \, p_k = - p_k \, p_i \qquad (i, k = 1, \ldots, n),$$

where $p_1 \ldots p_n$ are complex symbols [1]), and we introduce aequivalent complex symbols

$$(p_i)_1 = (p_i)_2 = (p_i)_3 = \ldots .$$

The same with q_{ik}.

According to the first principal theorem of the symbolical method any whole rational invariant of the given tensors is a sum of products of bracket-factors of the following form:

$$(p_1^2 \cdots p_\mu^2 \, p_{\mu+1} \cdots p_\nu \, q_1^2 \cdots q_\lambda^2 \, q_{\lambda+1} \cdots q_\varkappa \; {}_1a \ldots {}_\sigma a) \quad \mu + \nu + \lambda + \varkappa + \sigma = n. \quad (1)$$

For $\mu = \nu$ and $\lambda = \varkappa$ the bracket-factor is itself an invariant and we shall prove the

THEOREM: *The (smallest) complete system of invariants of the antisymmetrical tensors p_{ik} and q_{ik} and the vectors ${}_1a_i, \ldots, {}_ra_i$ are formed by the following brackets*

$$(p_1^2 \ldots p_\mu^2 \, q_1^2 \ldots q_\lambda^2 \; {}_1a \ldots {}_\rho a) \quad . \; . \; . \; . \; . \; . \; . \quad (2)$$

If the number of vectors is $\geqq n$, there are of course invariants without p and q, e.g. $({}_1a \ldots . {}_na)$. If n is even there are invariants without a's, to wit

$$(p_1^2 \ldots p_\mu^2 \, q_1^2 \ldots q_\lambda^2).$$

2. PROOF. We consider an invariant I consisting of a product of brackets and containing in particular (1) where $\mu \neq \nu$ and $\lambda \neq \varkappa$. Find the other bracket containing the symbol $p_{\mu+1}$ and transform by the aid of an identity of the symbolical method so that this 2nd symbol gets into (1). We find:

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[1]) Cf. R. WEITZENBÖCK. Invariantentheorie. Groningen (1923). Especially Abschnitt III.

$$\left.\begin{aligned}
&(2\mu+2)\,(p_1^2\cdots p_\mu^2 p_{\mu+1}\cdots p_\nu\; q_1^2\cdots q_\lambda^2 q_{\lambda+1}\cdots q_\varkappa\; {}_1a\cdots {}_\sigma a)\,(p_{\mu+1}\cdots)=\\
&=(-1)^{\nu-\mu}2\lambda(p_1^2\cdots p_{\mu+1}^2 p_{\mu+2}\cdots p_\nu q_1^2\cdots q_{\lambda-1}^2 q_\lambda\; q_{\lambda+1}\cdots q_\varkappa\, {}_1a\cdots {}_\sigma a)\,(q_\lambda\cdots)+\\
&+\sum_\pi(-1)^\pi\,(p_1^2\cdots p_{\mu+1}^2 p_{\mu+2}\cdots p_{\mu+\pi-1} p_{\mu+\pi+1}\cdots p_\nu\, q_1^2\cdots q_\lambda^2 q_{\lambda+1}\cdot\cdot q_\varkappa\, {}_1a\cdot\cdot {}_\sigma a)(p_{\mu+\pi}\cdot\cdot)+\\
&+\sum_\tau(-1)^{\nu-\mu+\tau}(p_1^2\cdot\cdot p_{\mu+1}^2 p_{\mu+2}\cdot\cdot p_\nu\; q_1^2\cdot\cdot q_\lambda^2 q_{\lambda+1}\cdot\cdot q_{\lambda+\tau-1} q_{\lambda+\tau+1}\cdot\cdot q_\varkappa\, {}_1a\cdot\cdot {}_\sigma a)(q_{\lambda+\tau}\cdot\cdot)+\\
&+\sum_\rho(-1)^{\nu-\mu+\varkappa-\lambda+\rho}(p_1^2\cdot\cdot p_{\mu+1}^2 p_{\mu+2}\cdot\cdot p_\nu q_1^2\cdot\cdot q_\lambda^2 q_{\lambda+1}\cdot\cdot q_\varkappa\, {}_1a\cdot\cdot {}_{\rho-1}a\, {}_{\rho+1}a\cdot\cdot {}_\sigma a)\,({}_\rho a\cdot\cdot).
\end{aligned}\right\}\quad(3)$$

We have written I as a sum of invariants where (1) is replaced by a bracket-factor which contains the square of one more symbol p. By continuing this we split I into invariants each of which contains a bracket-factor in which all the symbols p are quadratic. Finally we can obtain that the symbols p are quadratic in all the brackets. In this case all the brackets have the form:

$$(p_1^2\cdots p_\mu^2\, q_1^2\cdots q_\lambda^2 q_{\lambda+1}\cdots q_\varkappa\, {}_1a\cdots {}_\sigma a)\quad .\;.\;.\;.\;.\;.\quad (4)$$

We apply a similar transformation as (3):

$$\left.\begin{aligned}
&(2\lambda+2)\,(p_1^2\cdots p_\mu^2\, q_1^2\cdots q_\lambda^2\, q_{\lambda+1}\cdots q_\varkappa\, {}_1a\cdots {}_\sigma a)\,(q_{\lambda+1}\, p^2\cdots q^2\cdots q_\alpha\cdots a\cdots)=\\
&=-2\mu(p_1 p_2^2\cdots p_\mu^2 q_1^2\cdots q_\lambda^2 q_{\lambda+1}^2 q_{\lambda+2}\cdots q_\varkappa\, {}_1a\cdots {}_\sigma a)\,(p_1\, p^2\cdots q^2\cdot\cdot q_\alpha\cdot\cdot a\cdot\cdot)+
\end{aligned}\right\}.\quad(5)$$

+ terms which contain one symbol q more quadratically and which consist again of brackets of the type (4). We transform the first term once more by conveying p_1 out of the first bracket-factor into the second. In this way we split our invariant I' into invariants with brackets of the type (4) which contain either a symbol more quadratically or a bracket-factor that contains a symbol q more and a symbol p less quadratically than (4). If we continue this we get, apart from the invariants which contain a symbol more quadratically, invariants of which the 1st bracket-factor has the form

$$(q_1^2\cdots q_\lambda^2\, q_{\lambda+1}\cdots q_\varkappa\, {}_1a\cdots {}_\sigma a)\quad .\;.\;.\;.\;.\;.\;.\quad (6)$$

The last of these transformations leads to exclusively invariants that contain one symbol more quadratically, and of which the brackets have kept the type (4).

If we continue this long enough we obtain a whole rational function of brackets in which all the symbols are quadratic.

The form of the invariants shows directly that the complete system of invariants (2) cannot be replaced by a smaller one.

3. We shall now treat the case that, besides ${}_1a_i,\ldots,{}_ra_i,\ p_{ik}$ and q_{ik} an arbitrary number of contravariant vectors ${}_1u^i\ldots{}_su^i$ are given. In this case we have, besides (1), symbolical factors of the following types:

$$({}_{i_1}u' \dots {}_{i_n}u'), \qquad \dots \dots \dots \qquad (7)$$

$$({}_l a\ {}_h u'), \qquad \dots \dots \dots \qquad (8)$$

$$(p\ {}_h u') \qquad \dots \dots \dots \qquad (9)$$

and

$$(q\ {}_h u'), \qquad \dots \dots \dots \qquad (10)$$

where $i_1 \dots i_n$ are n numbers out of $1, \dots, s$ and $l = 1, \dots, r$, $h = 1, \dots, s$.

(7) and (8) are invariants; with (9) and (10) we form directly the invariants

$$(p\ {}_h u')\,(p\ {}_k u') \qquad \dots \dots \dots \qquad (11)$$

and

$$(q\ {}_h u')\,(q\ {}_k u') \qquad \dots \dots \dots \qquad (12)$$

where

$$h, k = 1, \dots, s, \quad h \neq k.$$

If now we choose again an invariant which is a product of symbolical factors, we may at once disregard factors of the types (7) and (8) and we need only consider the types (1), (9) and (10). Now the factors of type (1) can contain a symbol p of which the aequivalent symbol is contained in $(p\ {}_h u')$. Disregarding such symbols p and q, which we shall indicate resp. by π and ϱ, we can, according to the proof given above, reduce all the brackets of the type (1) to the more simple type

$$(p_1^2 \dots p_\mu^2\, q_1^2 \dots q_\nu^2\, \pi_1 \dots \pi_\lambda\, \varrho_1 \dots \varrho_\varkappa\ {}_1 a \dots {}_\sigma a) \qquad \dots \qquad (13)$$

In this case, however, the invariant that contains this factor, may be split into the product of 2 invariants of which one has the type

$$\left.\begin{aligned} &(p_1^2 \dots p_\mu^2\, q_1^2 \dots q_\nu^2\, \pi_1 \dots \pi_\lambda\, \varrho_1 \dots \varrho_\varkappa\ {}_1 a \dots {}_\sigma a)\,(\pi_1\ {}_1 u') \dots \\ &\qquad \dots (\pi_\lambda\ {}_\lambda u')\,(\varrho_1\ {}_{\lambda+1} u') \dots (\varrho_\varkappa\ {}_{\lambda+\varkappa} u'). \end{aligned}\right\} \quad (14)$$

We can continue in an analogous way with the other factor. There remains, therefore, only the invariant (14) to investigate. We transform all the $\varrho_\varkappa$ in the 1st factor. This fails only when at a given moment that first factor does not contain any π or p; in this case we have

$$(q_1^2 \dots q_\nu^2\, \varrho_1 \dots \varrho_\lambda\ {}_1 a \dots {}_\sigma a)\,(\varrho_1\ {}_1 u') \dots (\varrho_\lambda\ {}_\lambda u') \qquad \dots \qquad (15)$$

multiplied by invariants of the type (11). (15), however, gives invariants of the types (2) and (12).

Consequently there remains:

$$(p_1^2 \dots p_\mu^2\, q_1^2 \dots q_\nu^2\, \pi_1 \dots \pi_\lambda\ {}_1 a \dots {}_\sigma a)\,(\pi_1\ {}_1 u') \dots (\pi_\lambda\ {}_\lambda u') \quad \dots \quad (16)$$

We remark that $\lambda \leqq n$ and we may disregard those invariants (16) for which $2\nu \leqq \lambda$; in this case we transform all the q's out of the former factor into the latter.

THEOREM: *The smallest complete system of invariants of the antisymmetrical tensors* p_{ik} *and* q_{ik} *and an arbitrary number of covariant and contravariant vectors is*

$$({}_{l}a\ {}_{k}u'),\quad ({}_{i_1}u' \dots {}_{i_n}u'),\quad (p\ {}_{h}u')(p\ {}_{k}u'),\quad (q\ {}_{h}u')(q\ {}_{k}u'),$$

$$(p_1^2 \dots p_\mu^2\, q_1^2 \dots q_\lambda^2\ {}_{1}a \dots {}_{\sigma}a),$$

$$(p_1^2 \dots p_\mu^2\, q_1^2 \dots q_\nu^2\, \pi_1 \dots \pi_\lambda\ {}_{1}a \dots {}_{\rho}a)(\pi_1\ {}_{i_1}u') \dots (\pi_\lambda\ {}_{i_\lambda}u') \quad (2\nu > \lambda > 0;\ i_\alpha \neq i_\beta).$$

It remains still to show that this system is the smallest. For this we need only prove that an invariant of the latter type cannot be reduced to the other invariants by the aid of the symbolical identities. We can only transform one or another π in the 1st factor, through which, disregarding invariants with one square more, there arises an invariant with a factor $(\varrho u')$. We can only continue this with another π until all the symbols π are conveyed to the 1st factor. There remains, however, an invariant which does not belong to the indicated system, because, according to $2\nu > \lambda$, the first factor contains at least one symbol q.

4. We shall discuss a few special cases.

1. THEOREM: *The (smallest) complete system of invariants of an antisymmetrical tensor* p_{ik} *and an arbitrary number of vectors is*

$$({}_{l}a\ {}_{k}u') \qquad ({}_{i_1}u' \dots {}_{i_n}u') \qquad (p\ {}_{h}u')(p\ {}_{k}u')$$

$$(p_1^2 \dots p_\mu^2\ {}_{1}a \dots {}_{\sigma}a).$$

2. *If* 2 *covariant vectors* a_i *and* b_i *and no contravariant ones are given, we have for* $n = 2k$ *the complete system*

$$\left.\begin{array}{ll} (p_1^2 \dots p_i^2\, q_1^2 \dots q_{k-i}^2) & (i = 0, \dots, k) \\ (ab\,p_1^2 \dots p_i^2\, q_1^2 \dots q_{k-i-1}^2) & (i = 0, \dots, k-1); \end{array}\right\} \quad . \quad . \quad . \quad (17)$$

for $n = 2k + 1$

$$\left.\begin{array}{ll} (a p_1^2 \dots p_i^2\, q_1^2 \dots q_{k-i}^2) & (i = 0, \dots, k) \\ (b p_1^2 \dots p_i^2\, q_1^2 \dots q_{k-i}^2) & (i = 0, \dots, k). \end{array}\right\} \quad . \quad . \quad . \quad (18)$$

In both cases we have $n+1$ relative, hence n absolute invariants $I_1, \dots, I_n$. Accordingly all algebraic absolute invariants may be expressed in these n absolute invariants. As on the other hand, the given tensors and vectors have $2 \times \frac{1}{2} n(n-1) + 2n = n^2 + n$ independent components, we must get at least n independent absolute invariants through elimination of the coefficients of the transformation. Hence $I_1, \dots, I_n$ are n independent absolute invariants.

3. *If* 3 *covariant vectors* a_i, b_i *and* x_i *are given, we have for* $n = 2k$ *a complete system, which, besides of* (17), *consists of*

$$\left.\begin{array}{ll}(xap_1^2\dots p_i^2\,q_1^2\dots q_{k-i-1}^2) & (i=0,\dots,k-1)\\ (xbp_1^2\dots p_i^2\,q_1^2\dots q_{k-i-1}^2) & (i=0,\dots,k-1).\end{array}\right\}\quad\dots\quad(19)$$

For $n=2k+1$ we get besides (18)

$$\left.\begin{array}{ll}(xp_1^2\dots p_i^2\,q_1^2\dots q_{k-i}^2) & (i=0,\dots,k)\\ (xabp_1^2\dots p_i^2\,q_1^2\dots q_{k-i-1}^2) & (i=0,\dots,k-1).\end{array}\right\}\quad\dots\quad(20)$$

In the same way as above we find in both cases $2n$ independent absolute invariants. We find in particular n independent absolute invariants $(x\,{}_h\alpha')$, which we can also consider as covariants of the system a_i, b_i, p_{ik} and q_{ik}. Consequently the n contravariant vectors ${}_h\alpha^i$ are linearly independent.

We can also prove the latter by direct calculation of the determinant $D=|\,{}_h\alpha^i\,|$ on the supposition that for $n=2k$

$$I=(abq_1^2\dots q_{k-1}^2)\neq 0 \text{ and } I'=(p_1^2\dots p_k^2)\neq 0,$$

whereas all the other invariants op (17) are zero; in this case we find

$$D=c\,I^k\,I'^{k-1},\quad\text{where}\quad c\neq 0.$$

For $n=2k+1$ we calculate D in the same way by assuming

$$I=(a\,p_1^2\dots p_k^2)\neq 0\quad\text{en}\quad I'=(b\,q_1^2\dots q_k^2)\neq 0,$$

whereas all the other invariants of (18) are zero; in this case

$$D=c'\,I^k\,I'^k,\quad\text{where}\quad c'\neq 0.$$

4. *For 2 covariant vectors a_i and b_i and one contravariant vector u we find, besides (17) and (18), for $n=2k$ and $n=2k+1$ resp.*

$$\left.\begin{array}{lll}(a\,u') & (p\,u')\,(a\,p\,p_1^2\dots p_i^2\,q_1^2\dots q_{k-i-1}^2) & (i=0,\dots,k-2)\\ (b\,u') & (p\,u')\,(b\,p\,p_1^2\dots p_i^2\,q_1^2\dots q_{k-i-1}^2) & (i=0,\dots k-2)\end{array}\right\}\quad\dots\quad(21)$$

and

$$\left.\begin{array}{lll}(a\,u') & (p\,u')\,(p\,p_1^2\dots p_i^2\,q_1^2\dots q_{k-1}^2) & (i=0\dots,k-1)\\ (b\,u') & (p\,u')\,(a\,b\,p\,p_1^2\dots p_i^2\,q_1^2\dots q_{k-i-1}^2) & (i=0,\dots k-2)\end{array}\right\}\quad\dots\quad(22)$$

We find again $2n$ independent absolute invariants among which in particular n independent absolute invariants of the form $({}_h\beta\,u')$, which may be considered as contravariants of the system a_i, b_i, p_{ik} and q_{ik}.

Accordingly the covariant vectors ${}_h\beta_i$, defined in this way, are linearly independent. The minors of the determinant of these covariant vectors divided by the determinant give n linear independent contravariant vectors that depend linearly on the contravariant vectors ${}_h\alpha^i$ mentioned under 3.

5. Finally for $n = 4$ [1]) we have the

THEOREM: *The (smallest) complete system of invariants of* 2 *antisymmetrical tensors* p_{ik} *and* q_{ik} *and an arbitrary number of vectors is formed by*

$$({}_{l}a\ {}_{h}u') \qquad ({}_{i_1}u'\ {}_{i_2}u'\ {}_{i_3}u'\ {}_{i_4}u') \qquad (p_1^2\ p_2^2) \qquad (p^2\ q^2) \qquad (q_1^2\ q_2^2)$$
$$(p^2\ {}_{l}a\ {}_{m}a) \qquad (q^2\ {}_{l}a\ {}_{m}a) \qquad (p\ {}_{h}u')\,(p\ {}_{k}u') \qquad (q\ {}_{h}u')\,(q\ {}_{k}u')$$
$$(q^2\ p\ {}_{l}a)\,(p\ {}_{h}u').$$

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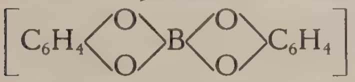
[1]) Cf. F. MERTENS. Invariante Gebilde von Nullsystemen. Wiener Berichte. Band XCVII (1888).

Chemistry. — *"On the Repulsive Action of Mutually Equal and Mutually Differing Groups in Saturated Organic Compounds."* By Prof. J. BÖESEKEN.

(Communicated at the meeting of February 28, 1925).

The increase of conductivity which boric acid undergoes in aqueous solutions through addition of ortho-dihydroxy-benzene derivatives, added to the separation of well-defined complex compounds of the type



$\left[C_6H_4{<}^{O}_{O}{>}B{<}^{O}_{O}{>}C_6H_4\right]K$, whereas this influence and this kind of compounds is absent in meta- and para-derivatives, renders it pretty well certain that this phenomenon should be ascribed in the first place to the particularly favourable position of the two hydroxyl groups in pyrocotechol and its derivatives.

That this increase of conductivity does not appear, or at least in a much smaller degree, in the aliphatic 1,2 glycols, will then be owing to the less favourable position which the OH groups occupy as a rule. Below we give once more a survey of the two categories of compounds, from which the difference will be at once clear.

Compare Table 1 next page.

We have assumed that in the aromatic nucleus the C-atoms with the groups bound to them, are held in one plane [1]), whereas in the saturated aliphatic compounds, in consequence of the revolvability of the molecule-parts round the single bonds as axes, the groups can assume a position imposed upon them by the mutually repulsive (and possibly sometimes also attractive) forces. The absence of an increase of the conductivity resp. the slight amount of it, might possibly also be attributed to the less acid character of the aliphatic compounds compared with that of the aromatic ones and the positive result in α-chlorhydrine might be an indication in this direction. That this difference can, however, have only a very small influence, appears particularly from the study of the cis-cyclopentanediol, and of the mannitan. These two are saturated aliphatic compounds, which distinguish themselves from α-glycols exclusively by their five-ring structure.

Through the presence of this ring the ring-forming atoms are held in one plane [1]), and the groups attached to them cannot easily yield to the mutually repulsive action. If therefore they lie on the same side of the ring these compounds must, if our deduction is correct, bring about a distinct increase of the conductivity of boric acid, which has, indeed, appeared very convincingly. (Table 1).

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[1]) The rigidity of the aromatic nucleus will be treated later on in connection with a corresponding slighter mobility of unsaturated compounds and of saturated ring-systems with at most five atoms.

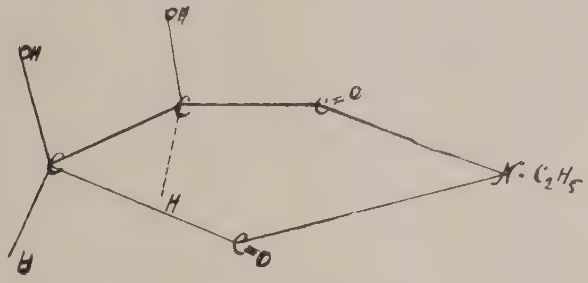
TABLE I.

Influence of a number of polyhydroxy-compounds on the conductivity of 0.5 mol. H_3BO_3 at 25°.

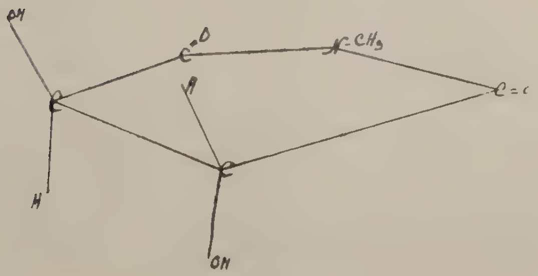
Compound	Conc.	Increase in Kohlr.-Holb. $\times 10^6$	Compound	Conc.	Increase in Kohlr.-Holb. $\times 10^6$
Pyrocatechol	$^1/_{32}$ mol.	104	Aethylene glycol	1 mol.	—
"	0.5 "	582	"	$^1/_{32}$ "	—
Resorcinol	0.5 "	—	Propylene glycol 1.2	0.5 "	—
Hydroquinone	0.5 "	—	α-Chlorhydrine	0.5 "	+ 5
Phloroglucinol	$^1/_{32}$ "	—	α-Methylether of glycerol	0.5 "	—
Pyrogallol	0.5 "	103			
"	$^1/_{32}$ "	573	χ-Phenylether of glycerol	$^1/_8$ "	± 0
Dihydroxy-naphtaline 1.2	$^1/_{32}$ "	65	Pinakone	0.25 "	+ 1
Protocatechuic acid	$^1/_{32}$ "	68	Divinyl glycol	0.5 "	—
Gallic acid	$^1/_{32}$ "	41	cis-Cyclopentanediol 1.2	0.5 mol.	about 150
Dinitropyrocatechol 3.5	$^1/_{256}$ "	122	trans- " 1.2	"	—
4. Nitroresorcinol	$^1/_{256}$ "	—	cis-Indandiol 1.2	$^1/_7$ "	63
Hydroxyhydroquinone	0.5 "	322	trans- " 1.2	" "	—
Gallic ac. methylester	$^1/_{32}$ "	212	*d*-Tartaric acid methyl-imide	0.2 "	—
Gallnut-tannin	$^1/_{213}$ "	230	Anti-tartaric-acid ethyl-imide	0.2 "	702
Dihydroxy-naphtaline 2.3	$^1/_{200}$ "	82	Mannitan	0.2 "	776

That it is entirely absent in trans-cyclopentane diol 1.2, may serve as counterproof. Remarkable is also the very different behaviour of *α*-methyltartrimide and anti-ethyltartrimide (see table 1 and figures on next page), from which it appears that the phenomenon is qualitatively independent of the rest of the molecule, when the ring consists of only five atoms.

We shall have to devote a few words to mannitan. We have already drawn attention in earlier publications to the fact that only in the *α*-glycols the two hydroxyl-groups, through mutual repulsion, can reach the most unfavourable position possible for seizing the boric acid molecule, viz. on opposite sides of the axis of the C-atoms to which they are bound. Going from ethylene glycol, via glycerol, erythrol, xylitol to mannitol,



Anti-aethylartrimide.



d-Methyltartrimide.

the position of two successive hydroxyl groups, even on mutual repulsion of all the hydroxyl groups, can never become so unfavourable as that in the simple α-glycols.

When we imagine the chain of the C-atoms to be a straight line, the two C-OH-bonds in the glycol will form an angle of 180° with each other, when we take only the repulsion of the OH-groups into account; in glycerol the three corresponding bonds can form at most an angle of 120°, in erythrol angles of 90° and in mannitol angles of 60°.

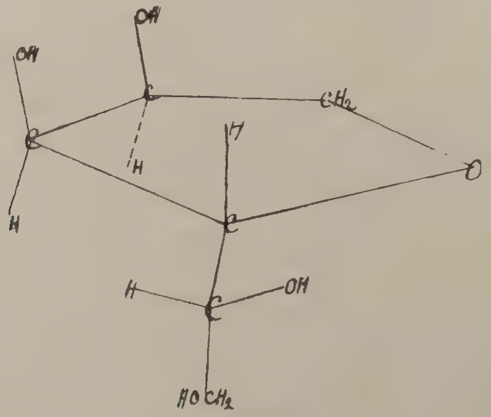
This way of representing the problem is certainly not correct, for the axis of the C-atoms is not straight, and in the poly-alcohols with four and more OH-groups these groups will not lie along a regular screw line; it may only serve to indicate that the mutual repulsion of a number of hydroxyl groups bound to adjoining C-atoms, must force these hydroxyl groups closer together as their number increases, and must thus lead them in couples to a more and more favourable position.

This appears to be actually the case on comparison of the action of glycol, glycerol, erythrol, and mannitol (dulcitol and sorbitol) on boric acid. (Table II). These values are the more striking when they are compared with those found for pyrocatechol (582) and pyrogallol (573), or for protocatechuic acid (68) and gallic acid (41), where a third OH-group does not bring about an increase of the influence (Table I) and where in view of the position of these groups in space, it was not to be expected either.

TABLE II.

Compound	Conc.	Increase
Aethylene-glycol	0.5 mol.	—
Glycerol	0.5 „	9
Erythritol	0.5 „	64
Mannitol	0.5 „	685
Dulcitol	0.5 „	720
Sorbitol	0.5 „	790
Mannitan	0.2 mol.	776
Mannitol	0.2 „	294

When mannitan and mannitol are compared, we see that in spite of the loss of two OH-groups, the influence of the boric acid is much greater, which must undoubtedly be attributed to the fact that the two OH-groups at the C-atoms 2 and 3, have yet become more accessible to the boric acid through their situation on the same side of the five-ring, than the *six* OH-groups in the mannitol.



Mannitan.

We need not devote much attention to the two OH-groups of the tail, because they can repel each other as far as possible just as in a simple α-glycol; we have indicated this in the symbol. Accordingly the α- and the β-methylglucoside, where the same tail is present, and for the rest also no hydroxyl groups with a favourable position, cause no increase of the conductivity of the boric acid.

While of the ethylene-glycol it is still possible to form a simple conception of the molecule in space, this becomes very difficult for the higher poly-alcohols. E. FISCHER's symbols, however excellent they may be to indicate the connection between them and the compounds to be derived from them, as sugars and hydroxylic acids, will bear but slight resemblance to the real state of equilibrium of the molecules in space. It is e.g. very well possible, and according to the measurements of the conductivity with boric acid even very probable, that the hydroxyl groups at the 2nd and 3rd or at the 4th and 5th C-atom do not lie closer to each other than any other pair of hydroxyl groups to the adjacent C-atoms. In this connection the study of the acetone compounds of mannitol is interesting. For it appeared from it that acetone combines most readily with the OH-groups at C_1 and C_2 (resp. C_5 and C_6), from which we conclude that this is the consequence of a not unfavourable position with respect to each other and of an easy accessibility, one of them being situated at the beginning of the molecule.

Further the fact that easily *three* acetone molecules, one of which at the OH-groups of C_3 and C_4, are absorbed, is of importance, because it appears from it that these too, though situated in the middle of the molecule, and as such certainly unfavourable, cannot lie so unfavourably with respect to each other, as FISCHER's symbol would lead us to expect.

It would, therefore, not be devoid of interest to separate the mannito-boric acid, and determine its composition and configuration.

We have here put the behaviour of mannitol towards acetone on a line with that towards boric acid. That this is allowed in aqueous acetone has appeared from investigations on the equilibrium:

$$\alpha\text{-glycol} + \text{acetone} \rightleftarrows \text{acetone compound} + \text{water},$$

of which it may be assumed in the case of analogous compounds that this will lie the more to the right as the hydroxyl groups in these glycols lie the more favourably [1]). It may appear from table III that actually the constants of equilibrium of the equilibrium considered above run pretty well parallel with the increase of the conductivity of 0,5 molar boric acid. Only monochlorhydrine is an exception, hence the chlorine atom brings about a disturbance.

At any rate it is clear that with exception of cis-cyclopentane diol 1,2, these glycols do not easily form a compound either with boric acid nor with acetone, so that we are really justified in assuming that this is to be ascribed in the first place to the less favourable position of the two hydroxyl groups with regard to each other.

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[1]) It is not allowed to apply this hypothesis indifferently to all polyhydroxy-compounds, because by the side of steric influences, also other influences will make themselves felt, especially when the nature of the molecules is very different. Compare: Onderzoek naar de ruimtelijke konfiguratie van enkele glykolen" by P. H. HERMANS, Proefschrift 1924.

TABLE III.

Glycol	K_{18°	Increase of conductivity
Aethylene glycol	0.14	— 1
α-Monochlorhydrine	0.28	+ 7.6
Propane1.2 diol	0.44	— 0.7
Propane 1.3 diol	0.026	— 4.0
Glycerol	0.74	+ 11.9
cis-Cyclopentanediol	$>$ 10.	+149.
cis-Cyclohexanediol	0.16	— 6.2
trans- „	0.00	— 8.4

And that they lie comparatively unfavourable is hardly to be explained in another way than by mutual repulsion, to which they can yield through the free rotation round the single bonds as axes, a repulsion which in the cases so far discussed is little opposed, if at all, by the other groups.

§ 2. With this repulsion of equal groups we have arrived at a hypothesis, which is accepted pretty generally, and which is supported by a number of observations. It is known of the carboxyl groups that they try to recede from each other as far as possible. Fumaric acid is stabler than maleic acid, and in the cyclic di-carbonic acids the cis-acid is for the greater part converted into the trans-acid on heating with acids.

This repulsion is also known of phenyl groups, as isostilbene (cis) can very easily been transformed to stilbene (trans).

As regards the glycols which are of interest here, only a few observations have been made, which confirm the mutual repulsion. In the preparation of *benzylantitartrimide* by heating benzylamine-antitatrate, it was found by J. COOPS ¹) that anti-amide with its hydroxyl-groups in the cis-position only produced a good yield below 115°; heating at 165° gave rise to the formation of much racemate (hydroxyl groups in transposition). The same observation was made for ethyl-antitartrimide: it was not even possible to prepare methyl-anti-tartrimide; when methylamine-anti-bitartrate was heated at 140°—145°, necessary to effect the ring-closure, exclusively the racemate resulted.

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¹) Proefschrift, Delft „De Stereoisomerie der wijnsteenzuren" pag. 60.

It was found by P. Hermans 1) that cis-hydrindene diol 1.2 and the two cis-tetrahydronaphtaline diols 1.2 and 2.3 likewise passed into their trans-isomers, when boiled with greatly diluted acids. This transformation appeared to be mutual.

As the position of the equilibrium was not the purpose of Hermans' research, and as the knowledge of it is required to form an opinion of the mutual stability, but as the determination of this equilibrium is disturbed by the transition, with splitting off of water, into cyclic ketones, it was examined whether the *heats of combustion* of cis-trans-isomer-compounds might possibly give some information on the mutual stability.

The following table gives a survey of reliable values from the literature, from which appears how insufficient these data are. The only reliable values point to a greater heat of combustion in the cis-isomers, which was also to be expected in view of these cases.

TABLE IV.

Heat of combustion of cis-trans isomer dicarbonic acid.

Compound	Mol. Heat of Combustion in Cal. (p. constant).	Δ
Fumaric acid 2)	320.3	6.1
Maleïc acid 2)	236.4	
Fumaric acid 3)	319.7	6.8
Maleic acid 3)	326.5	
Mesaconic acid 4)	477.4	2.5
Citraconic acid 4)	479.9	

A few more very accurate observations may be added to these. In the first place J. Coops 5), under guidance of Prof. Verkade, has burned some of the tartrimides prepared by him, and has found for the mol. heat of combustion (p. const.):

d-Ethyl tartrimide 671,1 d-Benzyl tartrimide 1237.8
Anti- „ 672.7 and Anti „ 1240.7.

Hence in both cases a positive difference for the cis- compared with the trans-isomer, for our purpose of more value than the values recorded in table IV, because it is here a question of α-diols. 6)

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1) Berichte **57**, 824 (1924).

2) Stohmann, Kleber and Langbein, Journ. pr. Ch. [2] **40** 202 (1889).

3) Landolt-Börnstein-Roth, Tabellen 1923 Tabel 331. Dissertatie Wallasch.

4) Stohmann, Zeitschr. f. physik. Ch. **10**, 412 (1892).

5) Proefschrift, Delft 1924 p. 141 and 148.

6) A positive difference never can give a *proof* of a lesser stability for there are cases known the stable isomer being formed with a negative heat-effect.

At my request Mr. and Mrs. VERKADE have determined the heats of combustion of cis- and trans-hydrindene diol 1,2 and of the two 1,2,3,4 tetrahydroxynaphthaline 1,2 diols:

		Δ
cis-Hydrindene diol 1.2	1098.5	1.8
trans- „	1096.7	
cis-1.2.3.4 Tetrahydronaphtaline 1.2 diol	1251.0	1.6
trans- „ „ „	1249.4	

With the greatest pleasure I avail myself of this opportunity to express my cordial thanks to the two investigators for their assistance. Here too the heat of combustion of the cis-modification is greater than of its trans-isomer.

It should, however, be borne in mind that these heats of combustion refer to the *solid* substances, and that we do not know the heats of melting. The melting-points of the trans-derivatives lie higher than the cis, hence the heats of melting are probably greater. To obtain perfectly comparable values, these would have to be added to the heats of combustion, which renders the difference cis-trans somewhat smaller. A reversal of the sign is, however, not to be expected, as, though the amount of the heat of melting is of the same order of magnitude (of benzene it is e. g. = 2,4 Cal.) we have to do with a difference of two heats of melting, which will certainly not differ much.

§ 3. *Influence of Other Groups on Each Other, and on the Hydroxyl Groups.*

It will be clear from the above that when the molecules at a chain or at a ring of five atoms bear only hydroxyl groups and hydrogen atoms, the mutual repulsion of the hydroxyl groups controls the state of equilibrium of the molecule.

This is changed when there are other groups in the molecule; even comparatively light groups, like methyl groups, will behave differently from hydrogen atoms.

This may e. g. appear from the heats of combustion of the two anhydrides of the symmetric dimethyl succinic acids determined by Mr. HARTMAN under guidance of Prof. VERKADE [1]):

$$\left.\begin{array}{llr} \text{i-dimethyl succinic acid anhydride} & \text{(cis)} & 681.0 \\ \text{r-} \;\; \text{„} \quad \text{„} \quad \text{„} \quad \text{„} & \text{(trans)} & 679.2 \end{array}\right\} \Delta = 1.8$$

---

[1]) Not published observation.

We see that the difference in the heat of combustion is of the same order of magnitude as that of the two hydrindene diols. (See Note 6, p. 377).

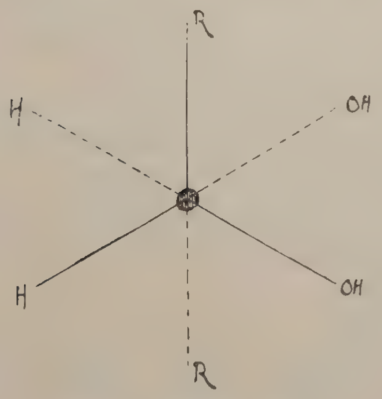
Without attaching too much value to this agreement, it is self-evident that the mutual repulsion will be of more importance between heavier groups, and especially between groups richer in electrons than between the hydroxyl groups.

The investigations by J. COOPS [1]) on the tartaric acids and their derivatives and those of P. HERMANS [2]) on the hydrobenzoins have proved this convincingly.

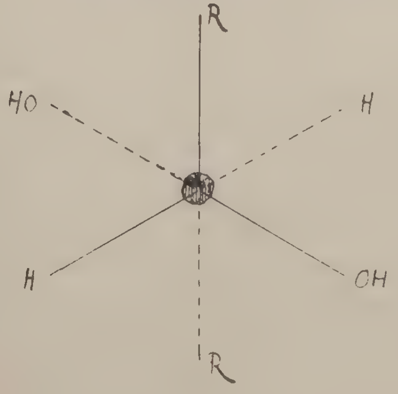
Mutual repulsion of the carboxyl groups.

In the *tartaric acids* a very great increase of the conductivity of boric acid was found in their character of α-hydroxy acids, the amount of which for the rest agrees with what was to be expected from a mono-substituted two-basic di-hydroxy acid [3]).

If it is, however, assumed that the mutual repulsion of the carboxyl groups considerably exceeds that of the other actions, the accumulation of carboxyl groups and hydroxyl groups in the active acids must be greater than in the inactive acid, as is shown in the above projections, in which the plane of projection is normal to the axis of the two central C-atoms.



Active or r-tartaric acid.



i-tartaric acid.

In consequence of this one-sided accumulation the chance to the formation of a boric acid compound in the active acids is increased, also because the hydroxyl groups are pressed closer together.

The measurements have confirmed this view, as may be derived from the subjoined table V of the observations.

We pointed out before that this configuration explains at the same time why racemic acid and its components are stronger acids than anti-tartaric acid, and why lactone-formation more readily sets in than that a normal internal anhydride is formed 1)).

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[1]) Proefschrif (loc. cit.) Delft.

[2]) Zeitschr. f. phys. Ch. **113**, 337—384 (1924).

[3]) Recueil **40** p. 579 (1921).

In the esters we have exclusively to do with the alcoholic hydroxyl groups; if here too the mutual repulsion of the carboxalkyl groups is greater than that of the hydroxyl groups, and if no other important disturbances interfere, the hydroxyl groups in the active (racemic) compounds will lie more favourably than in the inactive acids, as J. COOPS's 2)) investigations, indeed, show.

TABLE V.

Compound	Conc..	Increase of the conductivity of 0.5 Mol. H_3BO_3
d-Tartaric acid	$^1/_{16}$ mol.	4158
l- „	„	4120
Anti „	„	3750
d-Tartaric acid dimethyl ester	$^1/_5$ mol.	+ 10.0
„ diaethyl ester	„	+ 8.7
Anti tartaric acid dimethyl ester	„	— 1.8
„ diaethyl ester	„	— 5.9
r-Hydrobenzoin	$^1/_7$ mol. 3)	+ 10.
i- „	„ 3)	— 1

Mutual repulsion of the phenyl groups.

The same thing is found in the hydrobenzoins as in the tartaric acid esters. Here the differences are much greater. This appears indirectly from the measurements with boric acid: the value found for r-hydrobenzoin is apparently not greater, but the measurement could only be made in concentrated alcohol on account of the slight solubility of these substances in water, and in this the conductivity is very much less than it would have been in pure water; moreover the concentration is somewhat smaller.

The great difference in the configuration of the hydrobenzoins was particularly apparent in the determination of the position of the equilibrium of dissociation of the acetone compounds:

r-Hydrobenzoin: $K_{25} = 8.55$.
i- „ $K_{25} = 0.44$.

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1) These Proc. **29**, 368 (1920).

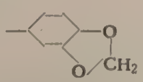
2) J. COOPS, Proefschrift (loc. cit.) p. 32—52.

3) These Proc. **33**, 29. These measurements had to be made in $72^0/_0$ alcohol, because the hydrobenzoins do not dissolve sufficiently in water; the conductivity in alcohol is very small.

Let us compare these values with those of the hydrindene diols 1.2. K_{18} for cis-hydrindene diol = 10.74 (for trans = 0.0 . . .) which glycols are to a certain extent comparable with the hydrobenzoins, then the hydroxyl groups in the r-hydrobenzoin must be situated very favourably with regard to each other.

This points to a repulsion between phenyl- and hydroxylgroups, which in the r-hydrobenzoin drives the hydroxyl groups still closer together, this action being neutralised by mutual compensation in the i-hydrobenzoin (see figures p. 379, in which R = phenyl). We will presently discuss a further proof of this repulsive action. Of the repulsion between the phenyl groups inter se indications had already been found by another

TABLE VI 1).

Name	Group R	Heat of Combustion per Mol. (p. constant)	Δ
Cinnamic acid	C_6H_5	1041.4	6.7
Allo cinnamic acid (58°)		1048.1	
p. Oxy cinnamic acid	C_6H_4OH (p)	992.4	5.1
Allo p. oxy cinnamic acid		997.5	
p. Methoxy cinnamic acid	$C_6H_4OCH_3$ (p)	1164.2	9.4
Allo p. methoxy cinnamic acid		1173.6	
Methyl cumaric acid	$C_6H_4OCH_3$ (o)	1162.4	6.2
Methyl cumarinic acid		1168.6	
Ethyl cumaric acid	$C_6H_4OC_2H_5$ (o)	1317.9	6.5
Ethyl cumarininic acid		1324.4	
Propyl cumaric acid	$C_6H_4OC_3H_7$ (o)	1472.0	6.0
Propyl cumarinic acid		1478.0	
Butyl cumaric acid	$C_6H_4OC_4H_9$ (o)	1632.4	6.4
Butyl cumarinic acid		1638.8	
i Amyl cumaric acid	$C_6H_4OC_5H_{11}$ (o)	1791.5	1.6
i Amyl cumarinic acid		1793.1	
Acetyl cumaric acid	$C_6H_4OCOCH_3$ (o)	1209.0	4.1
Acetyl cumarinic acid		1213.1	
Piperonyl acrylic acid		1068.8	9.0
Allo piperonyl acrylic acid		1077.8	

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1) Observations by ROTH and STOERMER, Berichte **46**. 267 (1913) and WALLASCH, Thesis for the doctorate Greifswald 1913. Compare also AUWERS, ROTH, and EISENLOHR, Annalen **407**, 126 (1914).

way; it is known, among other things, that isostilbene (cis) very easily passes into ordinary stilbene (trans), and in the melting of truxillic acids, i. e. diphenylcyclobutan dicarbonic acids, with caustic potash tranformations take place which can be accounted for in the simplest way by assuming that phenyl groups in the cis-position assume a trans-position.

The *repulsive action of the phenyl- on the carboxyl-group*, known from the transformation of allo- into ordinary cinnamic acid and their derivatives appears from the pretty considerable difference in the heats of combustion. (See Table VI p. 381).

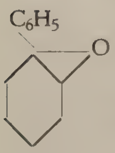
We have also been able to show this action in the phenylglycerol acids¹) by means of the boric acid method.

The high-melting acid (melting-point = 141°), obtained by oxidation of cinnamic acid methyl ester with $KMnO_4$ increases the conductivity more than the low melting acid (melting-point = 122°); there is in the former a greater accumulation of the OH-groups than in the latter, which should be the case when it is assumed that the phenyl- and the carboxyl-group repel each other more strongly than the two hydroxylgroups each other.

Repulsive action of phenyl- on hydroxyl group.

We mentioned just now a repulsive action between phenyl- and hydroxyl group, we have been accidentally able to show it in phenyl-1. cyclohexane diol 1.2.

In the preparation of this diol from the oxide through the action of diluted acid, the remarkable fact presented itself that chiefly the cis-diol was formed, whereas in all the other cases examined by us exclusively or chiefly trans-diol is formed²), which in itself is a very remarkable case of steric reversion.



On a closer examination it appeared to me that at first trans-diol is formed also here, which can very easily be changed into the cis-isomer even in the presence of very diluted acids.

It follows from this that the cis-diol is stabler than the trans-diol, which was, besides, corroborated by a every accurate combustion³).

The explanation lies in the repulsive action of the phenyl group at

	Heat of combustion	Δ
Phenyl 1 cis-cyclohexane diol 1.2	8132	4
„ 1 trans- „ 1.2	8136	

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[1]) Recueil **51**, 199—207 (1922).

[2]) Proefschrift CHR. VAN LOON. Delft 1919 pag. 73 en 78, Recueil **40**, 519—524, 530; **41**, 205, 333, 339.

[3]) This too was performed under the guidance of Prof. VERKADE by Mr. MAAN. (Compare however Note 6, page 377).

C-atom 1 on the hydroxyl group at C-atom 2, which is greater than between the hydroxyl groups at 1 and 2 inter se.

Action of the $CONH_2$-groups on each other and on the OH-groups. It remains to discuss the influence exercised by the *tartramides* on the conductivity of boric acid [1]). The subjoined table VII gives a survey of the measurements:

TABLE VII.

Compound	Conc.	Increase of the conductivity of 0.5 m. H_3BO_3 in Kohlr. Holb. × 10^6
d.-Tartramide	0.2 m.	+ 108.0
Anti-tartramide	„	35.7
d-Ethyl tartramide	„	91.6
Anti-diethyl tartramide	„	52.3
Malonic acid diamide	„	— 13.7

Here too it is seen that the active tartramide exerts a greater influence than the inactive so that the hydroxyl groups have again a more favourable position. Here, however, the explanation cannot solely lie in a preponderating mutual repulsion of the $CONH_2$-groups. If this were the case, the anti-tartramide could not undergo a considerable *positive* action from the boric acid. (See figures p. 384; then R is $CONH_2$).

This positive action cannot be owing to the $CONH_2$-groups as such or to a combination of them with a hydroxyl group, as the malic acid amide does *not* exert a positive action. The resultant of the forces between the different groups must here have as consequence that also in the anti-tartramide the hydroxyl groups lie pretty favourably.

For an explanation we may make the following suppositions:

1. The repulsive action of the OH-groups is not preponderant; this is self-evident, because otherwise they could not have a favourable position.

2. The repulsive action of the $CONH_2$-groups is not preponderant, because otherwise analogous phenomena would have been found as in the esters, i.e. no positive influence in the anti amide (see below).

3. When for the present we disregard attractive actions, it may be supposed that the $CONH_2$- and OH-groups repel each other with greater force than those groups each other, which renders the given configurations possible.

When the $CONHC_2H_5$-groups are further assumed to repel each other still less than the $CO\,NH_2$-groups, the OH-groups in the active amide,

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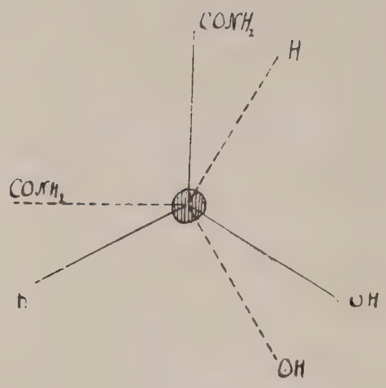
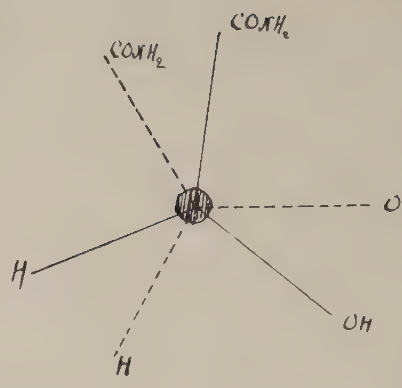
[1]) Proefschrift J. COOPS p. 52—55 and p. 46.



d-Tartramide.



Antitartramide.

would get somewhat further apart, in the inactive amide, however, somewhat closer together, which would then be in harmony with the values found by Coops (Table VII).

In view of the complexity of the problem and the lack of the required experimental material it is safer not to enter any further into the quantitative side of the problem.

Of this we may, however, be convinced that the mean position of equilibrium of the molecules is greatly dependent on *all* the modifications which both either the molecules themselves or the circumstances under which they are observed, undergo, and that e.g. the tartramides are, entirely differently orientated in space than the tartaric acids.

It is then obvious that the *rotary power* of optically active substances cannot be a *simple* function of the groups present in the molecule. Any change, however small it may seemingly be, changes the state of equilibrium of the molecule to such a degree, that for the present nothing can be predicted about the influence of a definite group on the amount of the rotatory power. The very extensive researches which have been made of late years in this region, have proved this convincingly. When we consider how entirely differently *d*-tartramide and *d*-tartaric acid are orientated in space, we see at once that the substitution of the basic NH_2-groups for the acid OH-groups must have a great influence on the rotation in *those* molecules, because the internal forces undergo a considerable modification. When, therefore, we wish to find regularities in this region, we must first of all consider the question: "What influence can the substitution of a definite group for an H-atom have on the state of equilibrium of the molecule?", in which the investigations by the boric acid and the acetone methods described here show us the way.

That the *principle of the optical superposition*, as it is often applied, is not valid, is clear without further discussion ¹): it may qualitatively have a certain value for the establishment of some regularities, quantitatively

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¹) Verslag Afd. Natuurk. Kon. Akad. v. Wet., **29**, 562—566.

it is sure to fall short, because the introduction of a new group brings a modification in the position of the atoms already present, just as the situation of the atoms of the introduced group undergoes a change of position through the atoms already present, and every displacement must cause a change in the amount of the rotation. The result is that placed over against the accurate investigations made of late the principle has proved entirely deficient ¹).

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¹) PATTERSON and TAYLOR, Journ. Ch. Soc. **87**, 33 (1905); PATTERSON and KAYE ibid. **89**, 1884 (1908) **91**, 705 (1907); PATTERSON and D. PATTERSON ibid. **107**, 142 (1915).

Chemistry. — *"The Constitution of the α-Eleostearinic Acid from Chinese Wood Oil and from its Isomer, the β-Eleostearinic Acid."* (Preliminary communication). By Prof. J. BÖESEKEN and Miss H. J. RAVENSWAAY.

(Communicated at the meeting of February 28, 1925).

The Chinese and Japanese wood-oils are obtained in China in great quantities, and used for caulking river boats, and stiffening textiles, for varnishing furniture and household things, etc.

Of late years these oils have become an important article of export, and they are put on the market in Europe in large quantities (in 1923: 80.000 tons).

They are very rapidly drying oils, polymerising on heating.

From a chemical point of view these oils occupy a particular place. Most oils are complicated mixtures of a pretty great number of glycerides; the wood-oils on the other hand consist for by far the greater part of one single glyceride of an unsaturated acid, the *α-eleostearinic acid,* which melts at 47° and can therefore easily be obtained in pure condition by recrystallisation. Besides under different influences this acid passes into a higher melting isomer, the *β-eleostearinic acid* (melting-point 67°), which is accordingly also easily accessible.

As the glyceride of wood-oil can be converted to the higher-melting glyceride of the β-eleostearinic acid by illumination (melting-point = 58°), a pure unsaturated glyceride has become easily obtainable.

By reason of the analysis and the iodine-value (160—170), the constitution of a linolic acid with two double bonds $C_{18}H_{32}O_2$ has been assigned to these eleostearinic acids, this acid having an uninterrupted chain of carbon atoms on account of its transition on reduction to stearinic acid.

As the tetrabromide of the acid, which could be obtained in very small quantities on bromination, was not identical with the tetrabromide from the linolic acid from linseed oil and poppyseed oil, it was assumed that the two double bonds occupied different places in the molecule [1]).

The ozonisation has yielded the result that 50 % of the quantity of valeric acid calculated would be formed, 75 % of that quantity of azelainic acid and further a small quantity of succinic acid [2]). From this the investigator concluded to the following formula:

$$CH_3(CH_2)_3CH : CHCH_2CH_2CH : CH(CH_2)_7COOH.$$

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[1]) B. H. NICOLET, Journ. Am. Chem. Soc. **43**, 938 (1921).
BAUER and HERBERTS, Chem. Umschau **29**, 229 (1922).

[2]) A. VERCRUYSSE, Bull. Soc. Chim. Belg. **32**, 151—156 (1923).

Now on examination of a sample of Chinese wood-oil I was struck with the very high index of refraction. This fact is very well known, for partly the identification of this oil is based on it, but no special significance was attached to it.

When however by the aid of LORENTZ's relation: $MR = \frac{n^2-1}{n^2+2} \cdot \frac{M}{d}$, we calculate the molecular refraction, and compare this value with that obtained by addition of the atomic refractions, on the supposition that the α-eleostearinic acid is an unsaturate acid with two double bonds, there appears to exist a very great exaltation, even when these double bonds are assumed to be conjugated. It is 17, resp. 12.

Spec. grav. 17	Refr. 17°	Mol. weight	Molecular Refraction		Calculated with 6 conjug. F
			Found	Calculat. + 6 F	
0.942	1.5220	878	284.6	267.6	± 273

The wood-oil itself being no pure glyceride, the β-glyceride was made by intensive illumination of the oil with the mercury lamp and purified by recrystallisation. Further were prepared the α- and the β-eleostearinic acid, and the ethylester of the α-eleostearinic acid.

The constants of these compounds and of the molecular refractions calculated from them, always on the supposition that they are acids or derivatives of acids with two double bonds, are the following:

Substance	Melt. point	Sp.Gr.	Refraction	Temp.	Molecular Refraction			Exaltation with regard to 2 F
					Calcul. for 2 F	Calcul. for 3 F	Found	
β-glycerine-ester	58°.5	0.8991	1.5051	80°	267.57	266.17	289.9	22.3
α eleostearinic acid aethyl-ester	 —	0.8968 0.9074	1.5038 1.5038	15° „	95.28 „	94.81 „	101.7 99.9	6.4 4.6
α eleostearinic acid..	47°	0.8980	1.5080	56°	86.04	85.57	93.05	7.0
β-eleostearinic acid..	67°	0.8839	1.4970	80°	86.04	85.57	92.80	6.8
linolic acid (from poppyseed oil	—	0.905	1.4710	15°	86.04	—	86.57	0.5

From this it appears convincingly that the exaltations are very great, they amount to between *five* and *seven* units for the *D*-line per unsaturated acid residue.

These amounts are exclusively met with in compounds with a succession of three conjugated bonds, as may appear from the following table:

Substance	Sp.Gr.	Refraction	Temp.	Molecular Refraction		Exaltation
				Found	Calculated	
Hexatriene [1].......	0.7369	1.5135	15°	32.78	28.49	4.29
Allo-ocimene [2].....	0.8132	1.5330	18°	52.83	46.97	5.86
Octatriene [2]........	0.7938	1.5456	10°8	42.49	37.74	4.75
Methyl 5-octatriene 1.3.5 [2]	0.8024	1.5335	18°	47.47	42.36	5.11

We accordingly arrive at the conclusion that a similar system of three double bonds is present in the eleostearinic acids.

To prove this both the wood-oil itself and the compounds prepared from it was hydrogenated by the aid of nickel powder; the following result was obtained:

Substance	Quantity in gr.	Absorbed H_2		Calculated H_2		Iodine value of hydrated substance	Temp. H_2
		c.c.	Mol.	c.c.	Mol.		
Wood oil.........	18.9	4050	7.9	4634	9	1.7	20°
,, ,, ...	18.5	3880	7.0	4481	9	3.1	15°
α-eleostearinic acid ether	16.7	3030	2.36	3863	3	2.9	20°
,, ,,	12.2	2630	2.79	2831	3	1.2	20°
,, ,,	12.5	2550	2.65	2894	3	1.1	18°
,, ,,	10.3	2150	2.82	2293	3	7.3	17°

In *all* cases actually much more hydrogen is absorbed than is calculated for two double bonds. It is true that not quite three molecules of hydrogen were absorbed per molecule of fatty acid [which in the wood-oil itself may be ascribed to the presence of less unsaturated components (among others oleic acid)], but these negative differences were on an average only 0,35 mol. in the recrystallised fatty acids and in the α-ethylester distilled in the cathode vacuum.

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[1] P. MULLER, Proefschrift Utrecht 1913.

[2] C. J. ENKLAAR, Recueil d. T. Ch. **36**, 215 (1917). Cf. also BÖESEKEN Koolwaterstoffen II pg. 58—66.

Though we cannot yet account for the cause of this shortage, we consider the presence of a conjugated system of three double bonds in the *pure* eleostearinic acids and their esters as proved.

In the first place this constitution explains the remarkably high refraction, further the exceedingly rapid drying, and the likewise very rapid polymerisation, both of the oil and of the free fatty acids.

Besides, on account of the formation of great quantities of azelainic acid on occidation, only the composition:

$$CH_3(CH_2)_3CH : CH . CH : CH . CH : CH(CH_2)_7COOH,$$

is possible, which is in perfect agreement with the presence of valeric acid [1]) as second important oxidation product in the action of ozon (loc. cit.). Only the formation of succinic acid, even though it be in small quantities, is less clear. For this reason a renewed investigation in this direction has been undertaken by us.

Finally the iodine-value seems in conflict with this conception; this is, however, only seemingly so, the investigations of the hexatrienes towards halogen having shown that they behave abnormally in this respect. (Dissertatie MULLER).

The details of this investigation and the further results will be published elsewhere.

Delft, February 1925.

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[1]) It may be pointed out here that MAQUENNE (Comptes Rendus **135**, 696 [1902]) had already shown that besides azelainic acid, valeric acid was formed in the oxidation of eleostearinic acid. By reason of his analysis he declared himself in favour of $C_{18}H_{30}O_2$; hence be considered it as an isomer of the linolenic acid, without, however, having proved this. To him the honour is due of having shown that β-eleostearinic acid is an isomer, and no polymer of the α-acid.

Mathematics. — "*Ueber projektive Differentialinvariauten*". V. Von Prof. R. WEITZENBÖCK.

(Communicated at the meeting of March 28, 1925).

Wir werden hier zeigen, dass die fünf letzten Tensoren der vorigen Mitteilung auf drei ($m = 2$), bzw. auf zwei ($m > 2$) projektive Tensoren reduzierbar sind[1]).

§ 1.

Wenn wir das Produkt $(Yy_1 \dots y_m Z_i) \, . \, y$ umformen, erhalten wir nach (66), IV (Gleichung (66) der vierten Mitteilung), d.h. also wegen

$$(v'Z_i) = (yy_1 \dots y_m Z_i) = 0$$

die Beziehung:

$$(Yy_1 \dots y_m Z_i)\, y = \sum_{\nu} (Yy_1 \dots y \dots y_m Z_i)\, y_\nu - (v'Y)\, Z_i \, .$$

Nun ist

$$(v'Y) = m \sqrt[m+2]{A},$$

also wird nach (70), (71) and (72), IV[2]):

$$mZ_i = -y\left(\sigma_i + \varepsilon_i^h \frac{N_h}{N}\right) + \varepsilon_i^h y_h \quad \dots \dots \quad (1)$$

Jetzt gehen wir aus von (59), IV:

$$mMy_{i(k)} = yp_{ik} + q_{ik}^{\rho} y_\rho + g_{ik} Z \quad \dots \dots \quad (2)$$

wo

$$\left.\begin{aligned} p_{ik} &= f_{ik} + mM_{i(k)} - mg_{ik}\frac{M^\rho M_\rho}{M} - mh_{ikl} M^l \\ q_{ik}^{\rho} &= mMh_{ik}^{\rho} + g_{ik} M^\rho, \end{aligned}\right\} \quad \dots \quad (3)$$

und bilden die Integrabilitätsbedingungen von (2) indem wir (2) nach t_l kovariant ableiten, dann k mit l vertauschen und subtrahieren.

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[1]) Dass bei $m > 2$ die dritte (quadratische) Fundamentalform im allgemeinen überflüssig wird, hat auch G. FUBINI bemerkt: Rend. Lincei V, **27** (1918), p. 150. Wie mir Herr BERWALD mitteilt, hat auch er 1923 unabhängig von FUBINI diese Tatsache festgestelt

[2]) Bei G. FUBINI, l.c., p. 148 ist gesetzt:

$$\lambda_i = -\left(\sigma_i + \varepsilon_i^h \frac{N_h}{N}\right) \text{ und } L_{ih} = \varepsilon_i^h \, .$$

Wegen

$$y_{i(k)(l)} - y_{i(l)(k)} = R^{\rho}_{i.kl}\, y_{\sigma}$$

haben wir:

$$\left.\begin{aligned} mM_l\, y_{i(k)} - mM_k\, y_{i(l)} + mMR^{\sigma}_{i.kl}\, y_{\sigma} = y\,[p_{ik(l)} - p_{il(k)}] + (y_l p_{ik} - y_k p_{il}) + {} \\ + y_{\rho}\,[q^{\rho}_{ik(l)} - q^{\rho}_{il(k)}] + (q^{\rho}_{ik}\, y_{\rho(l)} - q^{\rho}_{il}\, y_{\rho(k)}) + (g_{ik}\, Z_l - g_{il}\, Z_k). \end{aligned}\right\} \quad . \quad (4)$$

Hier können wir nun jedes $y_{\rho(\sigma)}$ vermöge (2) durch y, y_{ρ} and Z ausdrücken. Weiters lässt sich Z_l and Z_k nach (1) ausdrücken durch y und y_{ρ}. Hiedurch wird (4) eine lineare Beziehung zwischen den $m+2$ Punkten $y, y_1, \ldots, y_m$ und Z, die wegen (vgl. (47) und (48), IV):

$$(y y_1 \ldots y_m Z) = (v' Z) = mM \sqrt[m+2]{A} \neq 0$$

m + 2 einzelne Gleichungen ergibt. Davon ist eine von der Form $0 = 0$, nämlich diejenige, die man bekommt, wenn man die Keoffizienten von Z an beiden Seiten einander gleich stellt.

Der Koeffizient von y ergibt:

$$\left.\begin{aligned} \frac{M_l}{M} p_{ik} - \frac{M_k}{M} p_{il} = [p_{ik(l)} - p_{il(k)}] + \left(\frac{p_{\rho l}}{mM} q^{\rho}_{ik} - \frac{p_{\rho k}}{mM} q^{\rho}_{il}\right) - {} \\ - \frac{g_{il}}{m}\left(\sigma_l + \varepsilon^{\rho}_l \frac{N_{\rho}}{N}\right) + \frac{g_{il}}{m}\left(\sigma_k + \varepsilon^{\rho}_k \frac{N_{\rho}}{N}\right). \end{aligned}\right\} \quad . \quad . \quad (5)$$

Die Koeffizienten der y_{ρ}'s liefern:

$$\left.\begin{aligned} \frac{M_l}{M} q^{\rho}_{ik} - \frac{M_k}{M} q^{\rho}_{il} + mMR^{\rho}_{i.kl} = (p_{ik}\, \delta^{\rho}_l - p_{il}\, \delta^{\rho}_k) + (q^{\rho}_{ik(l)} - q^{\rho}_{il(k)}) + {} \\ + \frac{1}{mM}(q^{\sigma}_{ik}\, q^{\rho}_{\sigma l} - q^{\sigma}_{il}\, q^{\rho}_{\sigma k}) + \left(\frac{g_{ik}}{m} \varepsilon^{\rho}_l - \frac{g_{il}}{m} \varepsilon^{\rho}_k\right). \end{aligned}\right\} \quad . \quad . \quad (6)$$

Multiplizieren wir (6) mit g^{ik}, dann haben wir wegen

$$g^{ik}\left(\frac{g_{ik}}{m} \varepsilon^{\rho}_l - \frac{g_{il}}{m} \varepsilon^{\rho}_k\right) = \varepsilon^{\rho}_l - \frac{1}{m} \delta^k_l\, \varepsilon^{\rho}_k = \frac{m-1}{m} \varepsilon^{\rho}_l$$

wenn wir noch $m > 1$ voraussetzen und $g^{ik}\, R^{\rho}_{i.kl} = -R^{\rho}_l$ berücksichtigen:

$$\left.\begin{aligned} \frac{m-1}{m} \varepsilon^{\rho}_l = \frac{g^{ik}}{M}(M_l\, q^{\rho}_{ik} - M_k\, q^{\rho}_{il}) - mMR^{\rho}_l - g^{ik}\, p_{ik}\, \delta^{\rho}_l + {} \\ + g^{i\rho}\, p_{il} - g^{ik}(q^{\rho}_{ik(l)} - q^{\rho}_{il(k)}) - \frac{g^{ik}}{mM}(q^{\sigma}_{ik}\, q^{\rho}_{\sigma l} - q^{\sigma}_{il}\, q^{\rho}_{\sigma k}). \end{aligned}\right\} \quad . \quad . \quad (7)$$

Hiemit ist der Tensor ε^{ρ}_l durch g_{ik}, f_{ik}, h_{ikl} und die Invariante M ausgedrückt. Ist also M eine Invariante der drei Differentialformen g_{ik}, f_{ik} und h_{ikl}, so können wir sagen: ε^{ρ}_l ist auf diese drei Tensoren reduziert.

Setzen wir jetzt (7) in (6) ein, so entsteht ein System von Gleichungen

$$B^{\rho}_{i,kl} = 0 \quad \ldots\ldots\ldots\ldots \quad (8)$$

und die $B^{\rho}_{i,kl}$ sind hier aufgebaut aus den g_{ik}, f_{ik}, h_{ikl}, M und deren Ableitungen.

§ 2.

Wenn wir (5) mit g^{ik} multiplizieren, erhalten wir auf analoge Weise

$$\left.\begin{aligned}\frac{m-1}{m}\left(\sigma_l + \varepsilon^{\rho}_l \frac{N_\rho}{N}\right) = -\frac{g^{ik}}{M}(M_l p_{ik} - M_k p_{il}) + g^{ik}(p_{ik(l)} - p_{il(k)}) + \\ + \frac{g^{ik}}{mM}(p_{\rho l}\, q^{\rho}_{ik} - p_{\rho k}\, q^{\rho}_{il}).\end{aligned}\right\}. \quad (9)$$

Hier können wir nun von (7) Gebrauch machen und erhalten dadurch eine Beziehung, in der der Vektor σ_l ausgedrückt erscheint durch g_{ik}, f_{ik}, h_{ikl} und die beiden Invarianten M und N.

Setzen wir dagegen (9) in (5) ein, so erhalten wir ein System von Gleichungen

$$A_{i,kl} = 0, \quad \ldots\ldots\ldots\ldots \quad (10)$$

das mit $B^{\rho}_{i,kl} = 0$ zusammen die Integrabilitätsbedingungen von (2) darstellt.

Die explicite Gestalt von (8) und (10) in allgemeinen Koordinaten wird einigermassen kompliziert. In Normalkoordinaten dagegen haben wir, wenn wir auch noch $M = N = 1$ setzen, statt (3):

$$p_{ik} = f_{ik} \quad , \quad q^{\rho}_{ik} = m h^{\rho}_{ik}. \quad \ldots\ldots\ldots \quad (11)$$

Statt (7) kommt wegen $g^{ik} f_{ik} = 0$, $g^{ik} h^{\rho}_{ik} = 0$:

$$\frac{m-1}{m}\varepsilon^{\rho}_l = -mR^{\rho}_l + f_l^{\rho} + mg^{ik} h^{\rho}_{il(k)} - mg^{ik}(h^{\sigma}_{ik} h^{\rho}_{\sigma l} - h^{\sigma}_{il} h^{\rho}_{\sigma k})$$

$$\frac{m-1}{m}\varepsilon^{\rho}_l = -mR^{\rho}_l + f_l^{\rho} + mh^{\rho\nu}_{l(\nu)} + mh^{\sigma\nu}_l h^{\rho}_{\sigma\nu} \quad \ldots\ldots \quad (12)$$

Hieraus finden wir z.B. für die Invariante

$$\varepsilon^{\rho}_{\rho} = \varepsilon:$$

$$\frac{m-1}{m}\varepsilon = -mR + mh^{ikl} h_{ikl}\ ^{1)} \quad \ldots\ldots \quad (13)$$

(6) wird in Normalkoordinaten:

$$\left.\begin{aligned}mR^{\rho}_{i,kl} = (f_{ik}\delta^{\rho}_l - f_{il}\delta^{\rho}_k) + m(h^{\rho}_{ik(l)} - h^{\rho}_{il(k)}) + m(h^{\sigma}_{ik} h^{\rho}_{\sigma l} - h^{\sigma}_{il} h^{\rho}_{\sigma k}) + \\ + \frac{1}{m}(g_{ik}\,\varepsilon^{\rho}_l - g_{il}\,\varepsilon^{\rho}_k)\end{aligned}\right\} \quad (14)$$

---

¹) Bei affinen Differentialinvarianten und $m = 2$ findet sich diese Beziehung in W. BLASCHKE, Differentialgeometrie II, Springer (1923), Gleichung (146) auf 157.

und setzen wir hier (12) ein, dann erhalten wir die Gleichungen $B^{\rho}_{i,kl} = 0$ in Normalkoordinaten:

$$\left.\begin{aligned} B^{\rho}_{i,kl} = & -m(m-1)R^{\rho}_{i,kl} + (m-1)(f_{ik}\delta^{\rho}_{l} - f_{il}\delta^{\rho}_{k}) + m(m-1)(h^{\rho}_{ik(l)} - h^{\rho}_{il(k)}) + \\ & + m(m-1)(h^{\sigma}_{ik} h^{\rho}_{\sigma l} - h^{\sigma}_{il} h^{\rho}_{\sigma k}) + g_{ik}(-mR^{\rho}_{l} + f^{\rho}_{l} + mh^{\rho\nu}_{l(\nu)} + mh^{\sigma\nu}_{l} h^{\rho}_{\sigma\nu}) - \\ & - g_{il}(-mR^{\rho}_{k} + f^{\rho}_{k} + mh^{\rho\nu}_{k(\nu)} + mh^{\sigma\nu}_{k} h^{\rho}_{\sigma\nu}) = 0. \end{aligned}\right\} \quad . \quad (15)$$

Statt (9) haben wir:

$$\frac{m-1}{m}\sigma_l = -f^{\nu}_{l(\nu)} - f_{\rho\sigma} h^{\rho\sigma}_{l} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (16)$$

und (5) lautet nun:

$$(f_{ik(l)} - f_{il(k)}) + (f_{\rho l} h^{\rho}_{ik} - f_{\rho k} h^{\rho}_{il}) = \frac{1}{m}(g_{ik}\sigma_l - g_{il}\sigma_k). \quad . \; . \; . \quad (16a)$$

Mit Hilfe von (16) bekommen wir hieraus die Gleichungen $A_{i,kl} = 0$ in Normalkoordinaten:

$$\left.\begin{aligned} A_{i,kl} = & (m-1)(f_{ik(l)} - f_{il(k)}) + (m-1)(f_{\rho l} h^{\rho}_{ik} - f_{\rho k} h^{\rho}_{il}) + \\ & + g_{ik}(f^{\nu}_{l(\nu)} + f_{\rho\sigma} h^{\rho\sigma}_{l}) - g_{il}(f^{\nu}_{k(\nu)} + f_{\rho\sigma} h^{\rho\sigma}_{k}) = 0. \end{aligned}\right\} \quad . \; . \quad (17)$$

Hieraus finden wir, dass

$$A_{i,kl}\, g^{kl} = 0 \quad , \quad A_{i,kl}\, g^{ik} = 0 \quad , \quad A_{i,kl}\, g^{il} = 0. \quad . \; . \; . \quad (18)$$

Auf dieselbe Weise ergibt sich nach (15):

$$B^{\rho}_{i,kl}\, g^{kl} = 0 \quad , \quad B^{\rho}_{i,kl}\, g^{ik} = 0 \quad , \quad B^{\rho}_{i,kl}\, g^{il} = 0 \quad , \quad B^{i}_{i,kl} = 0; \quad . \quad (19)$$

dagegen finden wir durch Verjüngung bezüglich des Indizes ϱ und k:

$$\begin{aligned} B_{il} = B^{\rho}_{i,\rho l} = & -m(m-1)R_{il} - (m-1)^2 f_{il} - m(m-1)h^{\rho}_{il(\rho)} + m(m-1)h^{\sigma}_{\rho i} h^{\rho}_{\sigma l} + \\ & + (-mR_{il} + f_{il} + mh^{\nu}_{il(\nu)} + mh^{\sigma\nu}_{l} h_{i\sigma\nu}) - g_{il}(-mR + mh^{\sigma\nu}_{\rho} h^{\rho}_{\sigma\nu}) \end{aligned}$$

$$\left.\begin{aligned} B_{il} = & -m^2 R_{il} - m(m-2)f_{il} + mRg_{il} - m(m-2)h^{\nu}_{il(\nu)} + \\ & + m^2 h^{\rho}_{i\sigma} h^{\sigma}_{\rho l} - mg_{il}\, h_{\rho\sigma\nu} h^{\rho\sigma\nu} = 0, \end{aligned}\right\} \quad . \quad (20)$$

woraus sich für $m > 2$ die Beziehung ergibt:

$$(m-2)f_{il} = -mR_{il} + Rg_{il} - (m-2)h^{\nu}_{il(\nu)} + mh^{\rho}_{\sigma i} h^{\sigma}_{\rho l} - g_{il}\, h_{\rho\sigma\nu} h^{\rho\sigma\nu} = 0. \quad (21)$$

Ist $m = 2$, dann haben wir:

$$(R - h_{\rho\sigma\nu} h^{\rho\sigma\nu})\, g_{il} - 2R_{il} + 2h^{\rho}_{\sigma i} h^{\sigma}_{\rho l} = 0, \quad . \; . \; . \; . \; . \quad (22)$$

oder, da bei $m = 2$

$$R_{ik,lm} = \tfrac{1}{2} R(g_{il}\, g_{km} - g_{im}\, g_{kl}) \quad , \quad R_{km} = \tfrac{1}{2} Rg_{km}$$

ist [1]):

$$g_{il}\, h_{\rho\sigma\nu}\, h^{\rho\sigma\nu} = 2\, h^{\rho}_{\sigma i}\, h^{\sigma}_{\rho l} \quad \ldots \ldots \ldots \tag{22a}$$

Aus (20) folgt schliesslich noch:

$$B_{il}\, g^{il} = 0. \quad \ldots \ldots \ldots \tag{23}$$

§ 3.

Wir wollen die Gleichungen (20) und (21) auch noch in allgemeinen Koordinaten angeben. Dazu müssen wir (7) in (6) einsetzen und dann $\varrho = k$ nehmen. Einfacher ist es, wenn wir zuerst in (6) $\varrho = k$ setzen und dann die ε^{ρ}_{l} mit Hilfe von (7) eliminieren. Auf diese Weise ergibt sich aus (6) wegen

$$p_{ik}\, \delta^{k}_{l} - p_{il}\, \delta^{k}_{k} = (1-m)\, p_{il}:$$

$$\begin{aligned}(m-1)\, p_{il} = &- mMR_{il} - \frac{1}{M}(M_l\, q^{\rho}_{i\rho} - M_\rho\, q^{\rho}_{il}) + (q^{\rho}_{i\rho(l)} - q^{\rho}_{il(\rho)}) + \\ &+ \frac{1}{mM}(q^{\sigma}_{i\rho}\, q^{\rho}_{\sigma l} - q^{\sigma}_{il}\, q^{\rho}_{\sigma\rho}) + \frac{1}{m}(g_{i\rho}\, \varepsilon^{\rho}_{l} - g_{il}\, \varepsilon^{\rho}_{\rho}),\end{aligned}$$

also nach (7):

$$\left.\begin{aligned}(m-1)^2 . p_{il} = &- m(m-1)\, MR_{il} - \frac{m-1}{M}(M_l\, q^{\rho}_{i\rho} - M_\rho\, q^{\rho}_{il}) + \\ &+ (m-1)(q^{\rho}_{i\rho(l)} - q^{\rho}_{il(\rho)}) + \frac{m-1}{mM}(q^{\sigma}_{i\rho}\, q^{\rho}_{\sigma l} - q^{\sigma}_{il}\, q^{\rho}_{\sigma\rho}) + \\ + g_{i\rho}\Big[&\frac{g^{\mu\nu}}{M}(M_l\, q^{\rho}_{\mu\nu} - M_\nu\, q^{\rho}_{\mu l}) - mMR^{\rho}_{l} - g^{\mu\nu}\, p_{\mu\nu}\, \delta^{\rho}_{l} + \\ &+ g^{\rho\sigma}\, p_{\sigma l} - g^{\mu\nu}(q^{\rho}_{\mu\nu(l)} - q^{\rho}_{\mu l(\nu)}) - \frac{g^{\mu\nu}}{mM}(q^{\sigma}_{\mu\nu}\, q^{\rho}_{\sigma l} - q^{\sigma}_{\mu l}\, q^{\rho}_{\sigma\nu})\Big] - \\ - g_{il}\Big[&\frac{g^{\mu\nu}}{M}(M_\rho\, q^{\rho}_{\mu\nu} - M_\nu\, q^{\rho}_{\mu\rho}) - mMR - mg^{\mu\nu}\, p_{\mu\nu} + \\ &+ g^{\rho\sigma}\, p_{\rho\tau} - g^{\mu\nu}(q^{\rho}_{\mu\nu(\rho)} - q^{\rho}_{\mu\rho(\nu)}) - \frac{g^{\mu\nu}}{mM}(q^{\sigma}_{\mu\nu}\, q^{\rho}_{\sigma\rho} - q^{\sigma}_{\mu\rho}\, q^{\rho}_{\sigma\nu})\Big].\end{aligned}\right\} \tag{24}$$

Die Glieder mit p_{ik} auf der rechten Seite sind hier:

$$- g^{\mu\nu}\, p_{\mu\nu}\, g_{i\rho}\, \delta^{\rho}_{l} + g_{i\rho}\, g^{\rho\tau}\, p_{\sigma l} + (m-1)\, g_{il}\, g^{\rho\tau}\, p_{\rho\tau} = (m-2)\, g^{\mu\nu}\, p_{\mu\nu}\, g_{il} + p_{il}$$

Nach (3) und wegen $g^{\mu\nu}\, f_{\mu\nu} = 0$ wird dabei

$$g^{\mu\nu}\, p_{\mu\nu} = mg^{\mu\nu}\, M_{\mu(\nu)} - m^2\, \frac{M_\rho\, M^\rho}{M},$$

also unabhängig von f_{ik}. Auf der linken Seite von (24) steht also:

$$(m-1)^2\, p_{il} - p_{il} = m\,(m-2)\, p_{il}$$

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[1]) Bei affinen Invarianten: W. BLASCHKE, l. c. Gleichung (150) auf p. 157.

Auf der rechten Seite setzen wir

$$q^{\rho}_{ik} = mMh^{\rho}_{ik} + g_{ik}\, M^{\rho} \quad , \quad q^{\rho}_{i\rho} = M_i$$

ein und erhalten:

$$\left.\begin{aligned} m(m-2)\,p_{il} = &- m^2 MR_{il} + mMRg_{il} + m(m-2)\,g_{il}\, M^{\rho}_{(\rho)} - \\ &- m^2(m-2)\,g_{il}\,\frac{M_{\rho}\, M^{\rho}}{M} - m\,(m-2)\, Mh^{\rho}_{il(\rho)} + \\ &+ m^2\, Mh^{\sigma}_{\rho i}\, h^{\rho}_{\sigma l} - mMg_{il}\, h_{\rho\sigma\nu}\, h^{\rho\sigma\nu}. \end{aligned}\right\} \qquad (25)$$

Setzen wir hier schliesslich noch f_{il} aus (3) ein, so erhalten wir:

$$\left.\begin{aligned} (m-2)\,f_{ik} = &- mMR_{il} + g_{il}\,(MR + (m-2)\, M^{\rho}_{(\rho)} - Mh_{\rho\sigma\nu}\, h^{\rho\sigma\nu}) - \\ &- (m-2)\, Mh^{\rho}_{il(\rho)} + mMh^{\sigma}_{\rho i}\, h^{\rho}_{\sigma l} + m(m-2) M_{\rho}\, h^{\rho}_{il} - m(m-2)\, M_{i(l)}. \end{aligned}\right\} \qquad (26)$$

Diese Gleichung geht bei $m = 2$ über in (22), d.h. (22) und (22a) sind bei $m = 2$ auch in allgemeinen Koordinaten giltig und geben daher eine Beziehung zwischen den Tensoren g^{ik} und h_{ikl} unabhängig von den Koeffizienten der dritten Differentialform f_{ik}.

Bei $m = 2$ sind somit die Integrabilitätsbedingungen von (2):

1. Die Gleichungen $B^{\rho}_{i,kl} = 0$; sie enthalten g_{ik}, h_{ikl} und f_{ik}.
2. Die Gleichungen $A_{i,kl} = 0$: sie enthalten gleichfalls g_{ik}, h_{ikl} und f_{ik}.

Die Gleichungen (22) (ohne f_{ik}) stellen keine neue Bedingung für die Koeffizienten h_{ikl} vor, denn sie sind Identitäten zwischen den g_{ik}, h_{ikl} und deren Ableitungen. Es ist bei $m = 2$ nämlich immer möglich, durch eine Transformation $\tilde{y} = \lambda \,.\, y$ zu erreichen, dass $g_{11} = g_{22} = 0$ und $g_{12} = -1$ wird. Aber dann ist $R_{ik} = 0$, $R = 0$, $h_{112} = h_{122} = 0$ und (22) ist identisch erfüllt.

Ist dagegem $m > 2$, dann wird nach (21) oder auch nach (26) f_{ik} überflüssig und die Integrabilitätsbedingungen von (2) werden (wobei noch die p_{ik} nach (25) ausgedrückt sind):

1. Ein System von Gleichungen

$$^{\star}B^{\rho}_{i,kl} = 0,$$

das wir aus den Gleichungen $B^{\rho}_{i,kl} = 0$ bekommen, wenn wir in $B^{\rho}_{i,kl}$ die f_{ik} mit Hilfe von (26) ausdrücken.

2. Ein System von Gleichungen

$$^{\star}A_{i,kl} = 0,$$

auf dieselbe Art aus den Gleichungen $A_{i,kl} = 0$ erhalten.

$^{\star}B^{\rho}_{i,kl}$ und $^{\star}A_{i,kl}$ enthalten dann ausschliesslich g_{ik} und h_{ikl} und deren Ableitungen, vorausgesetzt, dass die Invariante M aus diesen Tensoren aufgebaut ist.

Chemistry. — *"Equilibria in systems in which phases, separated by a semipermeable membrane."* VIII. By F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of April 25, 1925).

The membrane-phase-rule and the membrane.

In the previous communication we have seen that an osmotic equilibrium:

$$E = E_1(n_1\, r_1) \mid E_2(n_2\, r_2) \quad . \;\; . \;\; . \;\; . \;\; . \;\; . \;\; . \;\; . \quad (1)$$

in which are present d substances, which diffuse by the membrane, has

$$(n_1 + n_2) - (r_1 + r_2) + 3 - d \quad . \;\; . \;\; . \;\; . \;\; . \;\; . \;\; . \quad (2)$$

freedoms. If we assume that both the separate systems E_1 and E_2 have the same pressure, then, therefore, equilibrium (1) has:

$$(n_1 + n_2) - (r_1 + r_2) + 2 - d \quad . \;\; . \;\; . \;\; . \;\; . \;\; . \;\; . \quad (3)$$

freedoms. We are able to deduce this and other properties also in the following way. Let us take f.i. the osmotic equilibrium:

$$E = L_1 \mid L_2 \quad . \;\; . \;\; . \;\; . \;\; . \;\; . \;\; . \;\; . \;\; . \;\; . \quad (4)$$

in which L_1 and L_2 represent two liquids;

L_1 contains the components $A_1\, B_1 \ldots XY \ldots UV$ and W . . (5)

L_2 „ „ „ $A_2\, B_2 \ldots XY \ldots UV$ and W . . (6)

Consequently both liquids contain the common components $XY \ldots UV$ and W; we assume that the d components UV and W are able to diffuse by the membrane, in contrary with the others viz. $XY \ldots$

Those components $XY \ldots$ behave, therefore, in both the liquids as if they are different substances; we may imagine them to be replaced in L_1 by the components $X_1 Y_1 \ldots$ and in L_2 by $X_2 Y_2 \ldots$; we then have two new liquids L'_1 and L'_2 in which

L'_1 contains the components $A_1\, B_1 \ldots X_1\, Y_1 \ldots UV$ and W . (7)

and

L'_2 „ „ „ $A_2\, B_2 \ldots X_2\, Y_2 \ldots UV$ and W . (8)

We now may imagine the osmotic equilibrium (4) to be substituted by the equilibrium:

$$E' = L'_1 + L'_2 \quad . \;\; . \;\; . \;\; . \;\; . \;\; . \;\; . \;\; . \;\; . \quad (9)$$

if we assume that only the components U V and W dissolve in both the liquid-phases. When in liquid L_1 [viz. in (5)] the number of components is n_1 and in liquid L_2 [viz. in (6)] the number is n_2, then follows from (7) and (8) that equilibrium (9) consists of $n_1 + n_2 - d$ components. Consequently, in accordance with the phase-rule of GIBBS, equilibrium (9) has:

$$(n_1 + n_2 - d) - 2 + 2 = n_1 + n_2 - d \text{ freedoms} \quad . \quad . \quad . \quad (10)$$

so that the osmotic equilibrium (4) has the same number of freedoms. This is also in accordance with the membrane-phase-rule; if we put viz. in (3) the number of phases $r_1 + r_2 = 2$, then (3) passes into (10).

We now make the same supposition for the components of system (1) as above for those of system (4); we then may imagine the osmotic equilibrium (1) to be replaced by the equilibrium:

$$E' = E_1' + E_2' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

which consists of $n_1 + n_2 - d$ components. As there are $r_1 + r_2$ phases, (11) and consequently also the osmotic equilibrium (1) has

$$(n_1 + n_2 - d) - (r_1 + r_2) + 2$$

freedoms; therefore, we refind (3).

Till now with our considerations we have made no supposition on the character of the membrane and on its action; we shall call a similar membrane, the character and action of which is not defined more closely, a "theoretical" membrane.

However, we may assume also that the membrane consists of a phase M, which, under definite conditions, permits some substance to diffuse, and other ones not; we shall represent this membrane, consisting of one phase M, by $| M |$ and call it a "real" membrane.

We now replace the theoretical membrane in (1) by a real membrane, so that we get the equilibrium

$$E = E_1 (n_1 r_1) + | M | + E_2 (n_2 r_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

We adjoin the following properties to this real membrane, consequently to the phase M:

1. It separates the two systems in such a way that the phases of E_1 do not come in direct contact with those of E_2;
2. It contains one or more substances $M N$ etc., which do not occur in the systems E_1 and E_2 and which do not dissolve in those systems;
3. From the substances, which occur in the systems E_1 and E_2, some are taken in by the membrane but others not; it forms with the taken substances a phase of variable composition.

We may imagine this real membrane f. i. as a solid solution or also as a thick, tuff, strongy viscous or jellied liquid or in another way. It stands to reason that it depends on the character of the membrane and on its strange substances MN etc. which substances will be taken in or not from the systems E_1 and E_2.

If we imagine for this real membrane a liquid, then theoretically this will probably be able to take in all substances from E_1 and E_2; practically, however, this need not be the case, the same f.i. a vapour does not contain practically all substances, which are present in the system, in which it participates.

We now are able to show: the real membrane $|M|$ which takes d substances from the systems E_1 and E_2, behaves like a theoretical membrane, by which these d substances may diffuse.

In order to show the above-mentioned, we firstly shall deduce the equations for equilibrium, which are valid for the osmotic equilibrium (1); for the sake of simplicity we assume that there is one diffusing substance only, viz. W.

We consider a system

$$E_A = A_1 + A_2 \ldots + A_r \quad \ldots \ldots \quad (13)$$

in which we give to an arbitrary phase A_i the composition:

$$A_i = x_i\, X + y_i\, Y + \ldots + w_i\, W \quad \ldots \ldots \quad (14)$$
$$i = 1, 2, \ldots r$$

We call ζ_i the thermodynamical potential of this phase A_i When this system E_A is in equilibrium, then must be:

$$\left.\begin{aligned} o = \frac{\partial\zeta_1}{\partial X} dx_1 + \frac{\partial\zeta_2}{\partial X} dx_2 \ldots + \frac{\partial\zeta_1}{\partial Y} dy_1 + \frac{\partial\zeta_2}{\partial Y} dy_2 \ldots \\ \ldots + \frac{\partial\zeta_1}{\partial W} dw_1 + \frac{\partial\zeta_2}{\partial W} dw_2 \ldots + \frac{\partial\zeta_r}{\partial W} dw_r \end{aligned}\right\} \quad \ldots \quad (15)$$

while the conditions:

$$\left.\begin{aligned} 0 &= dx_1 + dx_2 \ldots + dx_r \\ 0 &= dy_1 + dy_2 \ldots + dy_r \\ &\ldots\ldots\ldots \end{aligned}\right\} \quad \ldots \ldots \quad (16)$$

$$0 = dw_1 + dw_2 \ldots + dw_r \quad \ldots \ldots \quad (17)$$

must be satisfied.

From this we find in the known way the equations for equilibrium:

$$\frac{\partial\zeta_1}{\partial X} = \frac{\partial\zeta_2}{\partial X} = \ldots = \frac{\partial\zeta_r}{\partial X} \quad \frac{\partial\zeta_1}{\partial Y} = \frac{\partial\zeta_2}{\partial Y} = \ldots = \frac{\partial\zeta_r}{\partial Y} \text{ etc.} \quad \ldots \quad (18)$$

$$\frac{\partial\zeta_1}{\partial W} = \frac{\partial\zeta_2}{\partial W} = \frac{\partial\zeta_3}{\partial W} = \ldots = \frac{\partial\zeta_r}{\partial W} \quad \ldots \ldots \quad (19)$$

If A_1 is a phase of constant composition, viz. dx_1 and dy_1 satisfy the relations:

$$\frac{dx_1}{x_1} = \frac{dy_1}{y_1} = \ldots = \frac{dw_1}{w_1} \quad \ldots \ldots \quad (20)$$

then in (18) and (19) the terms with the index 1 disappear and we get a new equation:

$$\zeta_1 - x_1 \frac{\partial \zeta_k}{\partial X} - y_1 \frac{\partial \zeta_k}{\partial Y} \ldots - w_1 \frac{\partial \zeta_k}{\partial W} \quad \ldots \ldots \quad (21)$$

in which k represents one of the indices 2, 3 . . , r.

For a system:

$$E_B = B_1 + B_2 + \ldots \quad \ldots \ldots \quad (22)$$

of course similar equations are valid as for E_A, consequently equations, which correspond with (15) — (21); for this reason we shall call the equations, valid for E_A the equations (15 A) — (21 A), and those, valid for B, the equations (15 B) — (21 B).

We now are able to deduce the equations for equilibrium, which are valid for the osmotic equilibrium:

$$E = E_A \mid E_B \quad \ldots \ldots \quad (23)$$

in the following way. As now no more the thermodynamical potential of each of the separate systems E_A and E_B must be zero, but that of the complete system E, the equations (15 A) and (15 B) are no more valid each for itself, but we get:

$$0 = (15\,A) + (15\,B) \quad \ldots \ldots \quad (24)$$

the meaning of which is clear.

The changes $dx_1\, dx_2$ etc. which refer to the not-diffusing substances, satisfy the equations (16 A) and (16 B). As, however, the quantity of the diffusing substance W must not rest constant now in each of the separate systems E_A and E_B but it must in the complete equilibrium E the equations (17A) and (17B) disappear, therefore; they are substituted by the one equation:

$$0 = (dw_1 + dw_2 + \ldots)_A + (dw_1 + dw_2 + \ldots)_B = 0 \quad \ldots \quad (25)$$

Consequently for the osmotic equilibrium are valid the equations: (24), (25), (16 A) and (16 B).

If we deduce from this in the well-known way the equations for equilibrium, then we find:

the equations (18 A) and (18 B)

and still the equations:

$$\left(\frac{\partial \zeta_1}{\partial W} = \frac{\partial \zeta_2}{\partial W} = \ldots\right)_A = \left(\frac{\partial \zeta_1}{\partial W} = \frac{\partial \zeta_2}{\partial W} = \ldots\right)_B \quad \ldots \quad (26)$$

Those equations (26) involve not only the equations (19 A) and (19 B) but also still one new equation, viz.:

$$\left(\frac{\partial \zeta_k}{\partial W}\right)_A = \left(\frac{\partial \zeta_l}{\partial W}\right)_B \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (27)$$

in which, as follows from (26), we may take the indices k and l arbitrarily. Consequently we find for the osmotic equilibrium (23):

1^0 the equations for equilibrium, which are valid for each of the systems E_A and E_B separately;

2^0 besides a new equation for equilibrium viz. (27); this expresses that the osmotic water-attraction of both the systems E_A and E_B is equal.

We now consider the osmotic equilibrium:

$$E = E_A + |M| + E_B \quad . \; . \; . \; . \; . \; . \; . \; . \quad (28)$$

and we assume that the real membrane $|M|$ has the composition:

$$mM + nN + oO + \ldots + wW \quad . \; . \; . \; . \; . \; . \quad (29)$$

and the thermodynamical potential ζ. Instead of (24) we now get:

$$o = (15\,A) + \frac{\partial \zeta}{\partial W} \,.\, dw + (15\,B) \quad . \; . \; . \; . \; . \; . \quad (30)$$

This equation expresses that the thermodynamical potential of the complete system (28) must be a minimum. The variables dm, dn etc. of the strange substances $M\,N$ etc. of the membrane do not occur in this equation.

The equations (16 A) and (16 B), which refer to the not-diffusing substances of the systems E_A and E_B rest unchanged; equation (25), however, passes into:

$$o = (dw_1 + dw_2 + \ldots)_A + dw + (dw_1 + dw_2 + \ldots)_B \quad . \; . \quad (31)$$

this expresses that the quantity of the diffusing substance W, which is present in the complete system (28), remains constant. Consequently for system (28) we have the equations: (30), (31), (16 A) and (16 B).

If we deduce from this in the known way the equations for equilibrium, then we find, besides the equations (18 A) and (18 B) still also:

$$\left(\frac{\partial \zeta_1}{\partial W} = \frac{\partial \zeta_2}{\partial W} = \ldots\right)_A = \frac{\partial \zeta}{\partial W} = \left(\frac{\partial \zeta_1}{\partial W} = \frac{\partial \zeta_2}{\partial W} = \ldots\right)_B \quad . \; . \quad (32)$$

Those equations (32) involve not only the equations (26) but yet also a new equation, viz.

$$\frac{\partial \zeta}{\partial W} = \left(\frac{\partial \zeta_k}{\partial W}\right)_A \quad \text{or} \quad \frac{\partial \zeta}{\partial W} = \left(\frac{\partial \zeta_l}{\partial W}\right)_B \quad . \; . \; . \; . \; . \; . \quad (33)$$

in which we may take arbitrarily the indices k and l. Consequently we find for the equilibrium (28)

1^0 the same equations for equilibrium which are valid for the osmotic equilibrium (23)

2^0 besides a new equation (33); this expresses that the O.W.A. of the real membrane is equal to that of each of both the systems E_A and E_B separately. This equation defines also the concentration of the substance W in the membrane.

It appears from this, therefore, that the state of the separate systems E_A and E_B is defined by the same equations, immaterial whether those systems, as in (23) are in osmotic contact with the aid of a theoretical membrane, or, as in (28) with the aid of a real membrane.

Yet there may be any difference in the finishing-equilibrium of (23) and (28) if we start from definite systems (23) and (28). In the state of equilibrium of (28) viz. the real membrane must have a definite concentration of the substance W; had this concentration beforehand been different, then the membrane must take in a little water from the systems E_A and E_B or it has to give water to them. This quantity, and consequently also the influence on the final equilibrium, can be the greater, the greater is the mass of the real membrane. If the mass of the membrane is small with respect to that of E_A and E_B, then this influence may be neglected practically.

In the previous considerations we have supposed that each of the systems E_A and E_B contains one liquid at least. This is valid, however, also, if one of the systems consists of substances of constant composition, between which a phases-reaction may occur by taking in or giving water. If one of those systems consists f. i. of a solid substance X and its hydrate $X.n H_2O$, then on admittance of $\delta\mu$ quantities of water occurs the reaction:

$$\frac{\delta\mu}{n} \, . \, X + \delta\mu \, . \, H_2O \rightarrow \frac{\delta\mu}{n} (X \, . \, n \, H_2O),$$

consequently a reaction, with which the quantities of the phases change, but their compositions remain constant.

We now assume that in the system E_A on increase or loss of water a similar phases-reaction may occur. The increase of the thermodynamical potential on increase of $\delta\mu$ quantities of water, is represented by $\frac{\partial Z_A}{\partial W} . \delta\mu$ so that $\frac{\partial Z_A}{\partial W}$ defines the O.W.A. of system E_A.

For equilibrium (23) is valid now, instead of (24):

$$o = \frac{\partial Z_A}{\partial W} \, . \, \delta\mu + (15\,B) \quad . \; . \; . \; . \; . \; . \; . \; . \quad (34)$$

the equations (16 A) disappear, but (16 B) remain valid. Instead of (25) we now get, however;

$$o = \delta\mu + (dw_1 + dw_2 + . \, .)_B \quad . \; . \; . \; . \; . \; . \; . \quad (35)$$

If we deduce again from this the equations for equilibrium, then we find firstly the equations (18 *B*) and moreover:

$$\frac{\partial Z_A}{\partial W}=\left(\frac{\partial \zeta_1}{\partial W}=\frac{\partial \zeta_2}{\partial W}=\ldots=\frac{\partial \zeta_r}{\partial W}\right)_B \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

This contains not only the equations (19*B*) but still one equation more; this expresses that the O. W. A. of system E_A is equal to that of system E_B.

We now take, instead of equilibrium (23) with the theoretical membrane, equilibrium (28) with the real membrane. Then we have to replace (34) and (35) by:

$$o=\frac{\partial Z_A}{\partial W}\cdot d\mu+\frac{\partial \zeta}{\partial W}\cdot dw+(15\,B)$$

$$o=d\mu+dw+(dw_1+dw_2\ldots)_B.$$

We find from this again the same conditions for equilibrium (18 *B*) and also:

$$\frac{\partial Z_A}{\partial W}=\frac{\partial \zeta}{\partial W}=\left(\frac{\partial \zeta_1}{\partial W}=\frac{\partial \zeta_2}{\partial W}=\ldots=\frac{\partial \zeta_r}{\partial W}\right)_B.$$

Those last equations contain not only the equations (36) but moreover one, which expresses that the O. W. A. of the real membrane is equal to that of the systems E_A and E_B.

Consequently it appears from this that the deduced above on the correspondance of a system with a theoretical and a real membrane, is also true, if one of the separate systems consists of substances of constant composition, between which on increase or loss of water a phasesreaction occurs.

We may extend those considerations also to an osmotic equilibrium:

$$E=E_A+|\,E_0\,|+E_B$$

in which $|E_0|$ represents a real membrane, which consists of different phases and which has similar properties, as are discussed above for $|M|$. In similar way as above we find for this:

1^0. the equations for equilibrium, which are valid for each of the three systems E_A E_0 and E_B separately;

2^0. two equations, which express that the O.W.A. of the three systems is the same.

(To be continued.)

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Botany. — *"The Radium-growth-response of one cell."* By Prof. A. H. Blaauw and W. van Heyningen.

(Communicated at the meeting of February 28, 1925).

§ 1. *Introductory.*

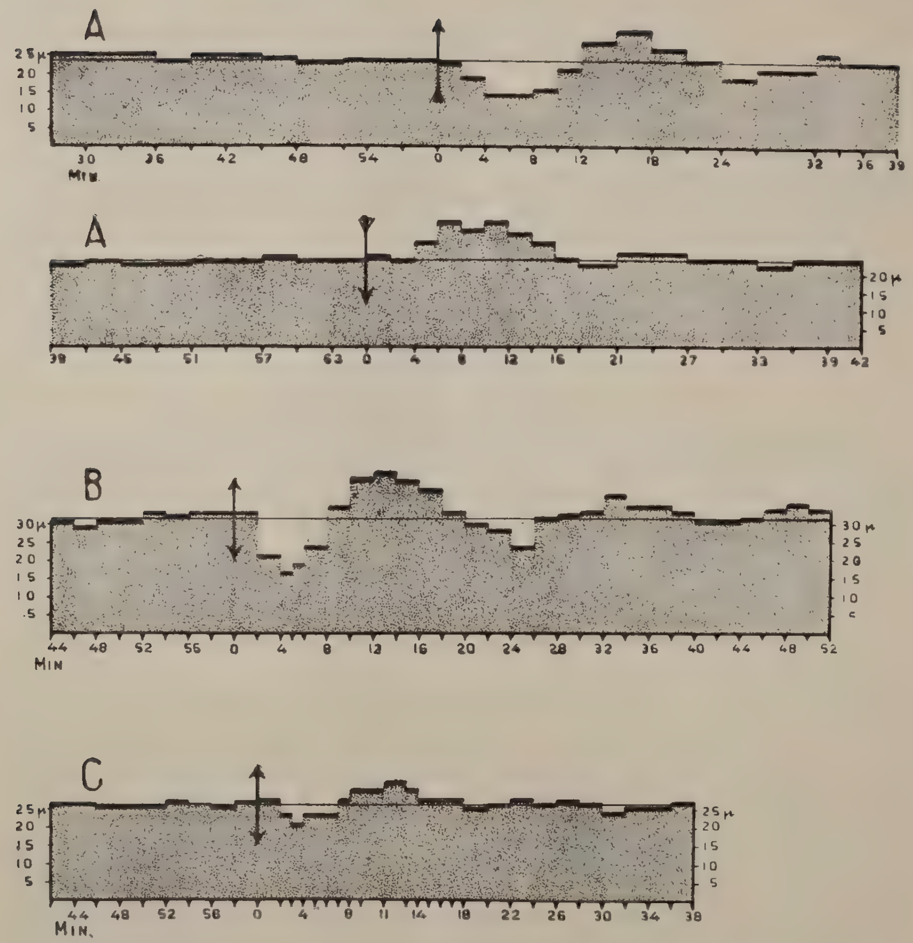
For some 10 years it has been known to us, that unicellular organs as the sporangiophores of *Phycomyces* and likewise various multicellular organs of higher plants respond to light-stimulations with characteristic accelerations and retardations of growth.

A joint discussion of the authors above-mentioned led to an investigation in the Laboratory for Plant-physiological Research at Wageningen, whether the growth of unicellular sporangiophores, so sensitive to visible light, is also affected by radium-rays.

Method. The experiments were made in a spacious dark room kept constantly at 17°—17.5° C., the temperature in which all previous light-investigations on *Phycomyces* were made. The cell was measured when it had reached a length of 3½—5½ cms. The mould-culture was cultivated in the same room and before the experiment it was placed for many hours in the centre of a small card-board house, partly soaked in paraffine, the wall being about 10 mms. thick. In order to observe the growth two red panes were inserted in front- and back-wall. All metal was avoided by using card-board, gum-paper and plasticine, in order to avoid secondary rays as much as possible, at least those of more penetrating power. For this purpose the culture in the card-board house and the radium-preparation (fixed on a *card-board* box) were placed in the middle of the room at 2 to 1½ metres distance from the stone wall and standing on high *wooden* tables. Radium-preparation, culture and horizontal microscope (magn. 70 ×), in which the metal could not be avoided, stood on separate tables on the concrete floor, which prevented all shaking or vibration of the tender long cells, the growth of which was to be measured.

The radium-preparation contained 9.55 mgrs. radium-element and was enclosed in a glass tube and a silver one, the latter 0.5 mm. thick. It was fixed on the cut-out rib of a small card-board box by means of a little plasticine or gum-paper. After the first experiments the silver tube (see below) was enclosed in a case of 2 mms. lead.

Whilst the growth of the mould-cell in faint red light was observed every 2 or 3 minutes through front and back-pane, the radium-preparation was placed at a certain moment at 10 or 5 cms. distance from the cell outside the



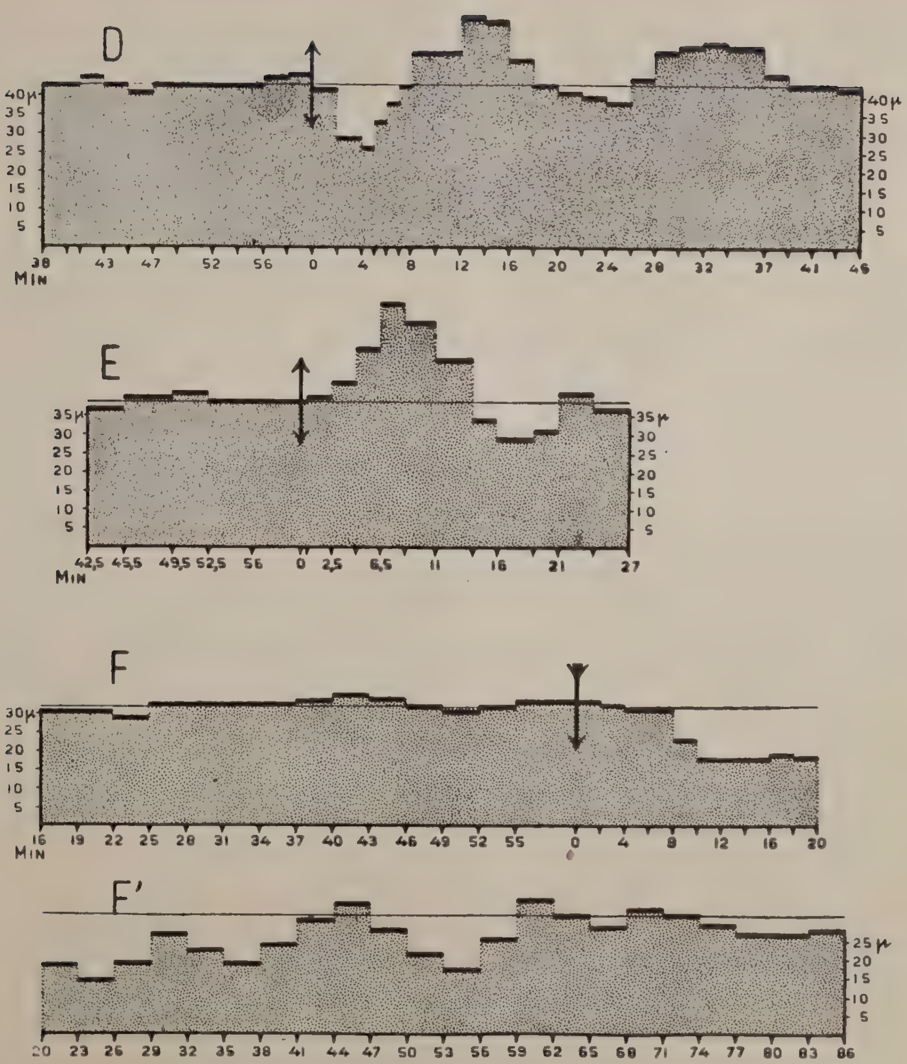
A *Radium-growth-response* in unintermitted exposure (66 min.) to 9,55 mgr. Ra-element at 10 cms distance from the cell (filters, see text). A′ a continuation of A with the response to removal of radium, i.e. the *radium-deradiation-response.*

B *Radium-growth-response* after 60 seconds and C after 5 sec. exposure at 5 cms distance from the cell.

The Reactions A, B and C occurred in the dark.

house for a shorter or longer time (see below), sending its rays through one of the side-walls and placed on the same level as the growing cell.

Tables and Figures. The tables concerning the growth (tables 1—23) first give the growth in dark before the exposure for 20—30 minutes in 10—12 observations ; the *growth of the cell in micron per minute* has been given in bold figures, i.e. the increase of length or growth averagely found during the period of time of 2—3 minutes between the points of time of observation, indicated by small figures. These periods of observation have been given in such a way that at the moment of exposure 60 is reached and we begin again at 0. Likewise at the end of an exposure of long duration the time begins at that moment at 0. Where the moment of beginning an



D *Radium-growth-response* of a cell, after 4-sided illumination for hours together with an intensity of 4 M.K. and exposed in that light for 60 sec. to the Ra-preparation at 5 cms distance (cf. B).

E Corresponding graphic representation of *response of growth to light* by M.K.S. (after one of the experiments of 1914).

F *Dark-growth-response* after 4-sided illumination in 4 M.K. for 5 hours, continued in F′.

exposure (↑) or ending an exposure (↓) does not coincide with an observation, the moment 0 with the arrow has been put between brackets.

The graphic representations have been construed in strict accordance with the tables. This time there has not been made a *natural* smooth curve as in previous publications, as is certainly more according to reality, but the average rate of growth during each period of time between two observations, has been indicated by a thick horizontal line. Every one can imagine the smooth curve as he thinks it most in accordance with reality. A thin straight drawn line indicates the rate of growth (according to the preceding observations) as it would have been, if no change of surroundings had occurred. Moments of observations have been indicated by dots against the abscis. Exposures of long duration begin at ↑ and eventually at ↓; exposures lasting 60 sec. or shorter have been indicated ↕.

§ 2. *Radium-growth-response. Result of exposure and of removal of radium (de-radiation).*

To begin with we subjoin 8 tables as a result of the first experiments. The cell was exposed at 10 cms. distance from a certain point of time for a long time or permanently. It was directly evident that these cells give a striking reaction to that exposure. Influence and reaction are outwardly perceptible in a characteristic response of growth. Of course this *radium-growth-response* is a secondary phenomenon as a result of more primary responses or modifications, brought about in the metabolism of the cell by the influence of the rays, but which are for the present absolutely beyond our understanding. These more profound, primary events brought about by radiation (light, radium or other rays) may be approximated more and more in means of growth-responses. The question is, whether in future in this sphere so dark to our understanding the biologist will meet the physicist and the chemist, who ascertain the most elementary properties of rays and matter from another viewpoint and give a foundation to the whole.

The *light-growth-response* (response to rays from the visible spectrum and the ultra-violet) is characterised in these cells by an acceleration of growth (positive response of growth) beginning after at least 3 minutes and changing into a temporal retardation of growth, etc. The *radium-growth-response is just contrary to the light-growth-response*, so negative, i.e. beginning with a strong decrease of growth, then on account of a contra-reaction passing into an acceleration of growth, while finally, also by permanent exposure the growth recovers its equability. Judging from these experiments, the rate of growth *averagely* becomes the same as before the exposure to *this* intensity. In order to be sure whether under the influence of permanent exposure the equable growth afterwards attained deviates some percents from the rate of growth before the exposure, a great number of long experiments is required to reduce the mean error sufficiently. It may be that larger quantities of radium placed nearer, will give more striking results in this respect. To answer all these questions further investigations will be wanted.

The radium-growth-response follows quicker than the light-growth-response; it is perceptible after an average of 2 minutes, the response to light averagely after 3½ minutes. The greatest depression after radium-exposure is reached after about 5½ minutes, the maximum of growth after light-exposure averagely after about 7 minutes (See tables 1—6) the summary in tab. 14, figure A compared to fig. E).

It should be pointed out here, that the cells of Phycomyces were subjected to one-sided exposure, that they never show a trace of curvatures, that on the other hand a strong growth-response follows on one-sided radium-exposure. But these rays are not refracted and they pass through these thin cells of such matter in such a way that there is no question of any practical difference of intensity within the cell. On account of this no unequal growth-response arises in the different sides of the growing zone of these cells and so no curvature is found. Refrangible light we have to supply on all sides, for if we supply on one side, the light-growth-response is found as well, but inequilateral on account of refraction of light and subsequent differences of intensity, and there soon appear the well-known phototropic curvatures.

Initially in the first experiments the glass tube containing the radium preparation was only enclosed in a silver tube, ½ mm. thick. Both the gamma-rays and a considerable part of the beta-rays could reach the cell through glass, silver and card-board. Soon after the silver enclosure was surrounded by 2 mms. lead to intercept the β-rays. To keep off the secondary β-rays caused in the lead-covering by the gamma-rays, a screen of 5 mms. aluminium was placed in front of it, and to intercept the fainter β-rays,which the gamma-rays should cause in the aluminium-layers, 10 mms. card-board were added. Even though in this way faint and soft secondary β-rays could not be absolutely avoided, yet at any rate by far the greater part of the β-rays were removed from the experiments while 80 to 90 % of the gamma-rays were preserved. The result was that the response was exactly the same, both as to nature and intensity. If a very great number of experiments were made and the intensity of response computed, taking the mean error into account, a slight decrease might be proved, the gamma-rays having also slightly lost in strength. But for the present our chief result is : *The radium-growth-response is caused by the gamma-rays, not by the beta-rays of the preparation.*

As a precaution it should be observed : 1. that the possibility exists that those gamma-rays indirectly exert this influence through β-rays secondarily formed outside or even inside the cell ; 2. that it is not impossible that these cells should show some sort of reaction to much stronger β-rays without gamma-rays.

In the further experiments the above-mentioned filter-layers 2 mms. Pb + 5 mms. Al. + 10 mms. cardboard, were always used.

After prolonged exposure the growth becomes steady fairly soon after an initially strong oscillation, so that the rate of growth observed in successive short periods varies no more than before the exposure (as a rule less than 10 %, which may be due to the method of observation or to natural slight oscillations). When this had been the case for a long time and the radium-growth-response was outwardly finished, the radium-preparation was removed. To be quite sure the rate of growth was observed for some time after and it suddenly appeared, that some minutes after the exposure had been stopped, a growth-response followed, the reverse of the radium-growth-response, beginning a little later and attaining its maximum acceleration somewhat later; the growth soon gets normal again. This was repeated several times after long exposures of various duration (47—159 minutes): the same phenomenon was repeated, of which the tables 3—8

TABLE 1. *Permanent exposure.*

23	32	26	29	29	$30^{1}/_{2}$	32	$30^{1}/_{2}$	35	$30^{1}/_{2}$	38	32	41	$30^{1}/_{2}$	44	$33^{1}/_{2}$
47	$33^{1}/_{2}$	59	32	53	31	56	$30^{1}/_{2}$	60 ↑	$30^{1}/_{2}$	2	**16**	5	**20**	8	31
10	35	12	35	14	35	17	**37**	20	**$41^{1}/_{2}$**	23	29	28	$26^{1}/_{2}$		
30	31	33	**24**	35	$29^{1}/_{2}$	38	37	41	32	44	$33^{1}/_{2}$	47	29	50	32
53	$29^{1}/_{2}$	56	32	59	$33^{1}/_{2}$	62	$33^{1}/_{2}$	65	32	68	32	72			

TABLE 2. *Permanent exposure.*

30	19	33	19	36	19	39	19	42	19	45	21	48	$21^{1}/_{2}$	51	20	54	21
57	21	60 ↑	19	3	**13**	6	**13**	9	$17^{1}/_{2}$	12	21	15	27	18	**29**	19	$25^{1}/_{2}$
21	25	24	21	27	**16**	30	25	33	$22^{1}/_{2}$	36	24	39	24	42	27	45	23
48	$26^{1}/_{2}$	51	27	54	24	57	23	60									

TABLE 3. *Permanent exposure and de-radiation after 49 minutes.*

43	$33^{1}/_{2}$	46	36	49	36	51	35	53	$33^{1}/_{2}$	55	$33^{1}/_{2}$	57	35
60 ↑	31	2	24	4	**$20^{1}/_{2}$**	6	$27^{1}/_{2}$	8	$33^{1}/_{2}$	10	43	12	**$45^{1}/_{2}$**
14	**$45^{1}/_{2}$**	15	43	17	$38^{1}/_{2}$	19	$38^{1}/_{2}$	21	37	24	36	26	36
28	36	30	36	32	$32^{1}/_{2}$	35	$33^{1}/_{2}$	37	$33^{1}/_{2}$	39	29	41	31
43	31	45	$32^{1}/_{2}$	47	35	49 ↓	$38^{1}/_{2}$	2	$37^{1}/_{2}$	4	37		
6	$44^{1}/_{2}$	8	**48**	10	**48**	12	36	14	35	16	$33^{1}/_{2}$	18	31
20	**$26^{1}/_{2}$**	22	31	24	36	26	36	28	36	30			

TABLE 4. *Permanent exposure and de-radiation after 66 minutes.*

27	$25^{1}/_{2}$	30	$25^{1}/_{2}$	33	$25^{1}/_{2}$	36	24	39	$25^{1}/_{2}$	42	$25^{1}/_{2}$	45	26	48	23
51	24	54	24	57	24	60 ↑	$23^{1}/_{2}$	2	19	4	**$14^{1}/_{2}$**	6	**$14^{1}/_{2}$**	8	**$15^{1}/_{2}$**
10	$21^{1}/_{2}$	12	29	15	**32**	18	27	21	24	24	**19**	27	$21^{1}/_{2}$	32	$26^{1}/_{2}$
34	24	36	24	39	23	42	24	45	23	48	23	51	24	54	24
57	25	60	24	63	24	66 ↓	25	2	24	4	29	6	**34**	8	**$31^{1}/_{2}$**
10	**34**	12	31	14	29	16	24	18	$22^{1}/_{2}$	21	$25^{1}/_{2}$	24	$25^{1}/_{2}$	27	24
30	24	33	$22^{1}/_{2}$	36	24	39	24	42							

TABLE 5. *Permanent exposure and de-radiation after 66 minutes.*

		27	28	31	29	33	30½	36	29½	39	28	42	27		
45	29½	48	30½	51	28	54	29	57	28	60 ↑	27	2	21½		
4	**17**	6	**19**	8	29	10	31	12	**33½**	14	**35**	16	31	18	24
21	**22½**	24	30½	27	**32**	30	30½	33	27	36	24	39	24	42	29
45	30½	48	28	51	26½	54	29	60	26½	63	26½	66 ↓	27½	2	29
4	31	6	31	8	**33½**	10	31	12	22½	14	23	16	24	18	**21**
21	24	25	24	27	21	30	24	33	24	36	25½	39	25½	42	25½
44	$25^{1}/_{0}$	50													

TABLE 6. *Permanent exposure and de-radiation after 114 minutes.*

36	38½	38	36	40	38½	42	38½	44	39½	46	40½	48	38½
50	36	52	36	54	38½	57	36	59	60 ↑ 38½	1	31½	3	**26½**
5	**26½**	6	**24**	7	30	8	41	9	38½	11	**48**	13	**48**
15	**47½**	17	44½	19	39	22	45½	24	35	27	33½	29	38½
31	33½	33	40½	35	40½	37	38½	39	40½	41	—	—	—
—	—	—	—	90	41	92	38½	94	41	96	41	98	39½
100	42	102	41	104	41	106	42	108	38½	112	38½	114 ↓	36
2	38½	4	47	6	51½	8	**55**	10	50½	12	41½	14	42
16	37½	19	33½	21	**31**	23	39½	25	41½	28	34½	30	36
32	33½	34	33½	36									

TABLE 7. *De-radiation after 110 minutes.*

—	— —	60	27	63	26½	66	26½	69	29	72	27	75	25½	78	28
81	26½	84	27	87	26½	90	27	93	29	96	29	99	28	102	27
105	28	108	27	110 ↓	26½	2	29	4	29	7	**38½**	10	**34½**	16	30½
19	29	22	26½	25	26½	28	28	31	24	34	28	37	25½	40	25½
43															

TABLE 8. *De-radiation after 72 minutes.*

0 ↑	—	— —	30½	— —	—	60	29	62	**32**	67	31	68	30
72 ↓	30	2	31	4	41	6	**45**	9	**43**	11	33½	13	**26½**
15	31	18	**36**	20	32½	22	27½	24	**25½**	22	(10 minutes delay)		
		37	29	38	31	42							

give instances. When after long exposure to radium the growth has become steady again, the radium-preparation cannot be removed without causing a new action contrary to the first. See fig. A′, a continuation of figure A.

This response which is the result of the removal (eventually decrease) of radiation, we shall call the de-radiation-response for shortness' sake. In our experiments it became, quite unexpectedly a complete corroboration and parallel of the *dark-growth-responses*, observed by TOLLENAAR (initially for Avena sativa already by SIERP) for various organs in a great number of experiments, as soon as a long exposure to light is stopped (eventually the intensity diminished). So the expression „de-radiation-response" is very comprehensive. The dark-growth-response is one and we can distinguish it in the case of radium as radium-de-radiation-response.

§ 3. *Short exposures.*

Summarizing tables.

In the way described above cells were also exposed for a short period, but at 5 instead of 10 cms. distance, i.e. with an intensity about 4 times stronger. On exposure for 60 seconds there arises a violent undulatory reaction, instances of which are given in tables 9, 10 and 11, while the experiment of tab. 10 is represented in fig. B.

But a still shorter exposure, for about 5 sec. i.e. with twelve times slighter quantity shows a much fainter yet clearly perceptible radium-growth-response. See tables 12 and 13 and fig. C. Here the average growth-depression amounts to about 20 % at the lowest point.

Another typical difference with the light-growth-response appears; whereas in that case after fainter radiation, i.e. with a decreasing response, the beginning of the response is perceptibly later, this is certainly not the case in the experiments on exposure to radium hitherto made. The much fainter response after 5 sec. is certainly not later; it is perceptible in the rate of growth after about 2 minutes.

Attempting to draw a comparison of its strength with the light-growth-response, we should be careful not to take the 40 % retardation of growth quantitatively as the opposite of 40 % acceleration of growth. In the case of light accelerations of growth of e.g. 200 % are caused in these cells with

TABLE 9. *60 sec. Exposure at 5 cms. distance.*

39	31	42	31	45	32	48	33½	51	31	54	34	57	31
60 ↕	32	2	25½	4	**19**	6	24	8	31	10	**41**	12	38½
14	38½	16	36	18	29	22	29	24	26½	26	29	28	26½
30	31	32	31	34	31	36	31	39	30	41	30	43	

TABLE 10. *60 sec. Exposure at 5 cms. distance.*

44	31	46	30	48	31	50	31	52	33½	54	32½
56	33½	58	33½	60 ↕	33½	2	21½	4	**17**	5	**19**
6	24	8	35	10	**43**	12	**44½**	14	**42**	16	39½
18	33½	20	30	22	29	24	**24**	26	32	28	32½
30	33½	32	**38½**	34	35	36	35	38	33½	40	31
42	31	44	32½	46	35	48	36	50	35	52	

TABLE 11. *60 sec. Exposure at 5 cms. distance*

37	31	39	33½	41	32½	43			33½	47	33½	49	32
52	30½	54	31	56	32½	58	31	60 ↕	33½	2	29	4	**24**
6	27½	8	35	10	35	12	**43**	14	**41**	16	37	18	38½
20	33½	22	29	24	30	27	31	29	32½	31	33½	33	33½
35	33½	37											

TABLE 12. *5 sec. Exposure at 5 cms. distance.*

38	38½	40	36	42	37	44	35½	48	38½	51	36	53	38½
56	36	58	36	60 ↕	36	2	31	4	**29**	5	**29**	6	**29**
7	38½	8	**43**	9	**43**	10	38½	12	41	14	41	16	36
18	37	20	31	22	36	24	33½	26	41	29	38½	31	41
33	36	35	36	37									

TABLE 13. *5 sec. Exposure at 5 cms. distance.*

42	27½	44	27½	46	26½	48	26½	50	26½	52	27½	54	27
56	26½	58	27½	60 ↕	29	2	24	3	**21½**	4	24	5	24
6	24	7	29	8	31	9	31½	11	**33½**	13	31	14	29
15	29	16	29	17	29	18	26½	20	27½	22	29	24	27½
26	26½	28	29	30	27½	32	25	34	26½	36	26½	38	27½
40													

small light-doses, whereas conversely a retardation of growth would have its maximum at 100 %, i.e. arrest if growth.

On the whole a retardation of growth indicates a stronger internal action than an acceleration of growth of equal percentage, especially according as the retardation (resp. acceleration) indicates a higher percentage. With the responses of growth an acceleration of 100 % is by no means quantitatively the reverse of 100 % retardation. The fainter the responses, the nearer we approach the limit of response, the better we can compare a positive and a negative response. Bearing this argument in mind, we may draw an approximate comparison for the following weak responses.

The radium-growth-response called forth by this preparation at 5 cms. distance for 5 sec. causes a retardation of growth of about 20 %, an exposure to ¼ M.K.S., 4-sided an acceleration up to about 20 %. Considering that the limit of a *perceptible* light-growth-response ("threshold") lies at about $^1/_{100}$ M.K.S., i.e. 25 times lower, the limit of the radium-growth-response will lie at about $^1/_5$ sec. under the circumstances described.

For comparison of light-growth-response and radium-growth-response a summarizing table follows. For comparison with 60 sec. radium-exposure, the results are used of radiations (4-sided) with light of 4 M.K.S., whilst in fig. E one of those experiments has been represented according to the figures found in 1913—1914.

TABLE 14. *Comparison of light- and radium-growth-responses after short exposures, at 17° C.*

	Average beginning of growth-response after at least	Maximum of response averagely	Maximum of response averagely after
4 M. K. S. 4-sided	$3^1/_2$ minutes	55 $^0/_0$ +	7 minutes
$9^1/_2$ mgrs. Ra-element at 5 cms., distance for 60 sec.	2 minutes	40 $^0/_0$ —	$5^1/_2$ minutes
$^1/_4$ M. K. S. 4-sided	$8^1/_2$ minutes	ca 20 $^0/_0$ +	11 minutes
$9^1/_2$ mgrs. Ra-element at 5 cms. distance for 5 sec.	2 minutes	ca 20 $^0/_0$ —	5 minutes

From the experiments hitherto made, nearly all rendered in the above tables, we summarize the cardinal points about period and strength of response in the tables 15, 16, 17 and 18.

TABLE 15.

	Beginning decrease rate of growth in the period:	Minimum rate of growth	Maximum rate of growth (anti-reaction)	2nd Minimum
Permanent exposure	3—6 Min.	3—9 Min.	18—19 Min.	
	3—6	3—6	12—15	
	2—5	2—5	20—23	
	2—4	4—8	15—18	
	2—4	4—6	14—16	
	0—2	4—6	13—15	
	1—3	5—7	13—15	
60 sec.	2—4	4—6	10—12	24—26 Min.
	2—4	4—5	12—14	24—26
	2—4	4—6	12—14	24—26
5 sec.	2—4	4—7	8—10	20—22
	2—3	3—4	11—13	
	1—3	5—7	—	

TABLE 16.

De-radiation after:	Beginning increase rate of growth in the period	Maximum rate of growth	Minimum rate of growth
49 Min.	?	8—12 Min.	20—22 Min.
66	4—6 Min.	6—12	—
66	?	8—10	18—21
72	4—6	6—11	13—15
110	7—10	7—10	—
114	4—6	8—10	21—23
159	3—6	6—10	—

TABLE 17.

	Decrease rate of growth 1st minimum	Increase rate of growth in maximum
Permanent exposure	35 per ct.	45 per ct.
	50	33
	40	33
	42	21
	40	33
	36	26
60 sec.	40	28
	48	33
	25	32
5 sec.	21	16
	22	22

TABLE 18.

De-radiation after	Increase rate of growth in maximum	Decrease rate of growth in minimum
49 Min.	33 per ct.	26 per ct.
66	41	6?
66	22	22
72	50	12
110	43	—
114	45	18

In connection with tables 14—18 we draw the attention to the following facts: 1. that the growth-responses are undulatory, the undulation gradually settling down into a steady growth, 2. that weak radium-growth-responses (in short exposures) do certainly not begin later as is the case with the light-growth-responses (see esp. table 14), 3. that the response to de-radiation undoubtedly begins a little later and reaches its maximum later than the response to radiation, exactly as was found in the case of the dark-growth-response.

§ 4. *Is the perception of light- and gamma-rays of a different nature?*

One principal question was most urging. Are light-growth-response and the response to gamma-rays, though contrary, yet identical as to their influence on the cell? For instance will organs, which contrary to *Phycomyces* show a negative light-growth-response, also respond contrary to *Phycomyces* as to the radium-growth-response? Or will all organs show a parallel response to gamma-rays? First the roots of *Sinapis alba* were exposed to rays at 5 cms. distance for 4 minutes. In spite of an extremely regular growth there was not the least indication of a radium-growth-response. But after all, this might very well be, though there was a relation between the influences of light- and gamma-rays. For the roots of *Sinapis* respond faintly to light; according to previous data they are at least 100.000 times less sensitive than *Phycomyces*-cells. For that reason the experiments were continued with *Helianthus*-germ-plants, which are at least 1000 times more sensitive to light. Here too the growth was extremely regular and could be accurately observed. The observations were continued for hours at a stretch. Nor was a trace of radium-growth-response to be found here.

On our considering the values previously found, we find that in *Helianthus* 4 M.K.S. causes a decrease of growth of not yet 10 %, 32 M.K.S. of averagely 23 %, in *Phycomyces* $\frac{1}{4}$ M.K.S. an increase of growth of about 20 % : 32 M.K.S. of 75 %. For *Helianthus* we approach with 4 M.K.S. the limit lying at about $^1/_{100}$ M.K.S. for *Phycomyces*. From these data we may conclude that roughly estimated the *Phycomyces*-cell needs about $^1/_{100}$ part of the light necessary for the *Helianthus*-germ-plant to give still a visible response; *Helianthus* therefore is about 80—100 times less sensitive to light than *Phycomyces*. The possibility remains, that on exposure to a much greater quantity of radium these germ-plants might show a directly perceptible response in their rate of growth. It may also be, that their non-reaction is due to quite different a mode of perception of light- and gamma-rays. On this subject the following experiments have been made.

Meanwhile the tables of *Helianthus* and *Sinapis* with perfectly even growth are left out for shortness' sake.

We know that the sensitiveness to light of the *Phycomyces*-cells in the dark is very great, but that it strongly decreases, when these cells are exposed (4-sided) to a constant, permanent intensity for a long period of time. The quantity of light which was to be supplied to cause a response of growth increases enormously, according as the intensity to which the cells are adapted, increases. While this limit lies in the dark at about 0.01 M.K.S., at 1 M.K. it has already risen to 25—50, at 8 M.K. to 200—400 MK.S.

Now let us put our cells for some hours in 4 M.K., then the sensitiveness is 10 to 20 thousand times slighter than in the dark.

As described and represented above the radium-growth-response at 5 cms. distance for 60 sec. was very vigorous. That is a radiation, which according to our above statement, is but about 300 times greater than the limit (ca $^1/_5$ sec.), at which a response would be barely perceptible. It is true that light and radium-growth-response are opposed, but it might be possible, that the perception, the initial influence of these rays was of identical character.

If the sensitiveness to radium has decreased as enormously, as the sensitiveness to light in 4 M.K., the exposure for 60 sec. (ca 300 times the limit in dark) would be absolutely insufficient to cause a response. Seeing the two reactions are opposed, it might be that after the diminution of light-sensitiveness, the possibility of radium-response might be greatly increased. They are all suppositions, only to be answered by experiments.

Tables 19, 20 and 21 refer to experiments, in which the cells were permanently exposed 4-sided to 4 M.K. and after 3½, and 4½ hours moreover to the radium-preparation at 5 cms. distance for 60 seconds. To attain this another card-board house was constructed with 4 mirrors in the corners for the lateral radiation of the cell with light from a 4-volt lamp. As on account of the mirrors the house had to be larger than in the previous experiments, there was made in the middle of the side-wall (for the sake of symmetry in both side-walls) a re-entering angle, to enable us to keep the preparation (and the interposed filters) outside the house, yet at 5 cms. distance from the cell.

With an illumination of 4 M.K., 4-sided, the sensitiveness to light being made 10.000 times slighter, the radium-growth-response continues the same.

Figure D pictures one of the 3 tables with the radium-growth-response in a intensity of 4 M.K., 4-sided. This figure D is directly comparable with figure B of the same response to radiation in the dark.

It is very probable that the initial influence of the light-rays and the gamma-rays (i.e. the perception of those rays viewed from the side of the plant-cell) is of quite a different nature or at least touches quite different a link of the process of metabolism. Only secondarily the results of both are shown in the modifications of the rate of growth described above.

TABLE 19. *Exposed to 4 M.K. 4-sided. After $3^1/_2$ hours 60 sec. Ra-exposure at 5 cms. distance*

24	$32^1/_2$	28	36	32	34	36	$33^1/_2$	38
	36	40	37	44	$33^1/_2$	47	35	50
	36	53	$33^1/_2$	56	35	59	(0 ↑)	32
2	**23**	4	**24**	6	36	8	**42**	10
	41	12	**41**	14	**42**	16	36	18
	$33^1/_2$	20	$33^1/_2$	22	31	24	32	28
	$33^1/_2$	31	$33^1/_2$	34	35	87	$30^1/_2$	40
	$30^1/_2$	43	29	46	32	49	32	52
	32	55	32	58	$33^1/_2$	61	35	64
	$34^1/_2$	67	32	70	$30^1/_2$	73	32	76
	$33^1/_2$							

TABLE 20. *Exposed to 4 M.K. 4-sided. After 4½ hours 60 sec. Ra-exposure at 5 cms. distance*

38	43	40	43	41	45	43	43	45	41	47	43	49
	43	52	43	54	43	56	45	58	45½	0 ↑		
	42	2	**29**	4	**26½**	5	33½	6	38½	7	43	8
	51½	10	51½	12	**61**	14	**60**	16	49½	18	43	20
	41	22	40	24	**38½**	26	44½	28	51½	30	**53**	32
	54	34	**53**	37	45½	38	43	41	43	43	42	45
	38½	47	43	49	41	52	42	54	41	56	45½	58
	48	60	43	62	45½	65	41	67	45½	69	49	71

TABLE 21. *Exposed to 4 M.K. 4-sided. After 4 hours 60 sec. Ra-exposure at 5 cms. distance.*

34	58½	36	58½	38	58½	40	55	42	53
44	57½	46	55	48	53	50	53	52	53
54	55	56	55	59	57½	0 ↑	57½	1	57½
2	**43**	3	**43**	4	45½	5	62½	6	72
7	**79**	9	**76½**	11	70½	12	67	14	62½
16	55	19	62½	21	60	23	59	25	57
26	64	30	62½	32	62½	34	57	38	62½
42	60	46							

TABLE 22. *Exposed to 4 M.K. 4-sided for 6 hours, next darkness.*

28	43	30	43	32	42	34	38½	36	43	39
	41	41	42	43	41	45	45½	47	48	49
	43	51	45½	54	41	56	45½	58	49 ↓	0
	48	2	43	4	38½	6	33½	8	**24**	10
	29	12	**24**	14	**26½**	16	33½	18	36	20
	44	23	33½	24	31	29	31	29	**26½**	31
	33½	33	33½	35	38	37	36	39	29	52
	31	43	36	45	35	47	41	49	51	52
	43	54	43	56	36	59	29	61	33½	63
	33½	65								

TABLE 23. *Exposed to 4 M.K. 4-sided, for 5 hours next darkness.*

0	$33^{1}/_{2}$	2	$33^{1}/_{2}$	4	31	6	32	8	$33^{1}/_{2}$	10	$33^{1}/_{2}$	13
	35	16	$30^{1}/_{2}$	19	$30^{1}/_{2}$	22	29	25	32	28	32	31
	32	34	32	37	$33^{1}/_{2}$	40	35	43	34	46	32	49
	$30^{1}/_{2}$	52	32	55	$33^{1}/_{2}$	0 ↓	$33^{1}/_{2}$	2	$32^{1}/_{2}$	4	31	6
	31	8	23	10	**18**	12	**18**	10	**18**	16	19	18
	$18^{1}/_{2}$	20	$18^{1}/_{2}$	23	**$14^{1}/_{2}$**	26	19	29	27	32	$22^{1}/_{2}$	35
	19	38	24	41	$30^{1}/_{2}$	44	35	47	28	50	$21^{1}/_{2}$	53
	$17^{1}/_{2}$	56	$25^{1}/_{2}$	59	36	62	32	65	29	68	$33^{1}/_{2}$	71
	32	74	$29^{1}/_{2}$	77	27	80	27	83	28	86		

In these latter experiments we availed ourselves of the opportunity to withdraw the light-rays from the cells, which had been exposed for 5 and 6 hours to 4 M.K., after recovering from the 60 sec. Ra-exposure. In the experiments of tables 22 and 23 and in figure F (with a continuation F′) a repeated corroboration may be found of a vigorous *dark-growth-response* after the growth has been adapted to a constant supply of light.

It stands to reason that here we have only just touched upon the subject of this striking radium-growth-response. Many new questions have arisen, into which the investigations should be continued. This narrow compass does not allow of discussing the question whether a comparison with other known physiological results of similar exposures is possible. This however is certain and may be important for human physiology and therapy, that the growth of these cells is an extremely sensitive measure or indicator for judging a physiologic effect of the gamma-rays and may be of other rays and thus for the quantitative comparison of such radiations different in intensity, in distance, in time, continuous or intermittent.

We are indebted to Miss FOLMER of Groningen for her kindness in giving us some technical hints with respect to mounting.

Wageningen
Den Haag, January 1925.

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Physics. — *"The Intensities of the* ZEEMAN*-Components"* 1). By S. GOUDSMIT and R. DE L. KRONIG. (Communicated by Prof. P. EHRENFEST).

(Communicated at the meeting of February 28, 1925).

By the aid of the correspondence-principle formulae have been given by SOMMERFELD and HEISENBERG 2) for the intensities of the ZEEMAN-components for the case of large quantum numbers. These formulae have been expressed in the quantum numbers by LANDÉ 3).

If for the initial state the quantum numbers considered here are J_1 and m_1, for the final state J_2 and m_2, the formulae for transversal observation are:

For the case that $J_2 = J_1 + 1$

$$\left.\begin{array}{lll} m_2 = m_1 + 1 & i_+ = A(\bar{J} + \bar{m})(\bar{J} + \bar{m}) & , \sigma \\ m_2 = m_1 & i_0 = 4A(\bar{J} + \bar{m})(\bar{J} - \bar{m}) & , \pi \\ m_2 = m_1 - 1 & i_- = A(\bar{J} - \bar{m})(\bar{J} - \bar{m}) & , \sigma \end{array}\right\} \quad . \; . \; . \; . \quad (1)$$

For the case that $J_2 = J_1$

$$\left.\begin{array}{lll} m_2 = m_1 + 1 & i_+ = B(\bar{J} + \bar{m})(\bar{J} - \bar{m}) & , \sigma \\ m_2 = m_1 & i_0 = 4B\,\bar{m}^2 & , \pi \\ m_2 = m_1 - 1 & i_- = B(\bar{J} + \bar{m})(\bar{J} - \bar{m}) & , \sigma \end{array}\right\} \quad . \; . \; . \; . \quad (2)$$

in which $\bar{J}$ and $\bar{m}$ express that it is uncertain whether in these formulae the quantum numbers of the initial or of the final state, or of an intermediate mode of motion should be used.

ORNSTEIN and BURGER 4) drew up the rule that the energy emitted by one of the magnetic levels of the initial state towards the final state, is equal for all these levels, on account of the equal-probability of the levels in a magnetic field. The same thing will hold for the energies which arrive at the magnetic levels of the final state. For the application

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1) Preliminary communication in Naturwiss. **13**, 90, 1925.

H. HÖNL. arrives independently at the same results in ZS. f. Phys. **31**, 340, 1925. Cf. also an article by R. DE L. KRONIG, which will shortly be published in ZS. f. Phys.

2) A. SOMMERFELD and W. HEISENBERG ZS. f. Phys. **11**, 131, 1922.

3) BACK-LANDÉ. ZEEMANeffect u. Multiplettstruktur p. 52.

4) L. S. ORNSTEIN and H. C. BURGER. ZS. f. Phys. **28**, 135 and **29**, 241, 1924.

of this rule it should be borne in mind that in the transversal observation only half the energy of the circularly polarized components finds expression. Hence ORNSTEIN and BURGER'S rule gives:

$$2i_{+} + i_0 + 2i_{-} = C \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

It seemed now natural to examine whether this relation, in connection with the formulae (1) and (2), might possibly be able to yield the intensities also for small quantum numbers. For this purpose different methods may be adopted, one of which will be discussed in what follows.

In connection with formulae (1) and (2) it will be expected that for small quantum numbers for $J_2 = J_1 + 1$

$$\left.\begin{array}{lll} m_2 = m_1 + 1 & i_{+} = A(J_1+m_1+a_1)(J_1+m_1+a_2) = & A(m_1^2+\alpha_1 m_1+\alpha_2) \\ m_2 = m_1 & i_0 = -4A(J_1+m_1+b_1)(J_1+m_1+b_2) = & -4A(m_1^2+\beta_1 m_1+\beta_1) \\ m_2 = m_1 - 1 & i_{-} = A(J_1+m_1+c_1)(J_1+m_1+c_2) = & A(m_1^2+\gamma_1 m_1+\gamma_2) \end{array}\right\} \quad (4)$$

In these formulae the intensities are expressed in the quantum numbers of the initial state, whereas the constants α, β, γ are independent of m. If we fill in the last members of these expressions in (3), and if we require the result to be independent of m, then

$$\alpha_1 - 2\beta_1 + \gamma_1 = 0 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

If in fig. 1, where the case $J_1 = J_2 + 1$ is diagrammatically represented, the virtual components on the edge of the scheme are considered, then

$$i\,(p) = A\,\{(J_1 + 1\tfrac{1}{2})^2 + \gamma_1\,(J_1 + 1\tfrac{1}{2}) + \gamma_2\} = 0$$
$$i\,(q) = A\,\{(J_1 + \tfrac{1}{2})^2 + \gamma_1\,(J_1 + \tfrac{1}{2}) + \gamma_2\} = 0$$

from which follows

$$\underline{\gamma_1 = -2\,(J_1 + 1)} \qquad \underline{\gamma_2 = (J_1 + \tfrac{1}{2})\,(J_1 + 1\tfrac{1}{2})}.$$

In the same way it is found that

$$i\,(\bar{p}) = A\,\{(J_1 + 1\tfrac{1}{2})^2 - \alpha_1\,(J_1 + 1\tfrac{1}{2}) + \alpha_2\} = 0$$
$$i\,(\bar{q}) = A\,\{(J_1 + \tfrac{1}{2})^2 - \alpha_1\,(J_1 + \tfrac{1}{2}) + \alpha_2\} = 0$$

hence

$$\underline{\alpha_1 = 2\,(J_1 + 1) = -\gamma_1} \qquad \underline{\alpha_2 = (J_1 + \tfrac{1}{2})\,(J_1 + 1\tfrac{1}{2}) = \gamma_2}.$$

The result $\alpha_1 = -\gamma_1$ and $\alpha_2 = \gamma_2$ might already have been arrived at from the symmetry of the ZEEMAN resolutions. With (5) this yields

$$\underline{\beta_1 = 0.}$$

Finally

$$i\,(r) = -4A\,\{(J + \tfrac{1}{2})^2 + \beta_2\} = 0$$

yields

$$\underline{\beta_2 = -(J_1 + \tfrac{1}{2})^2.}$$

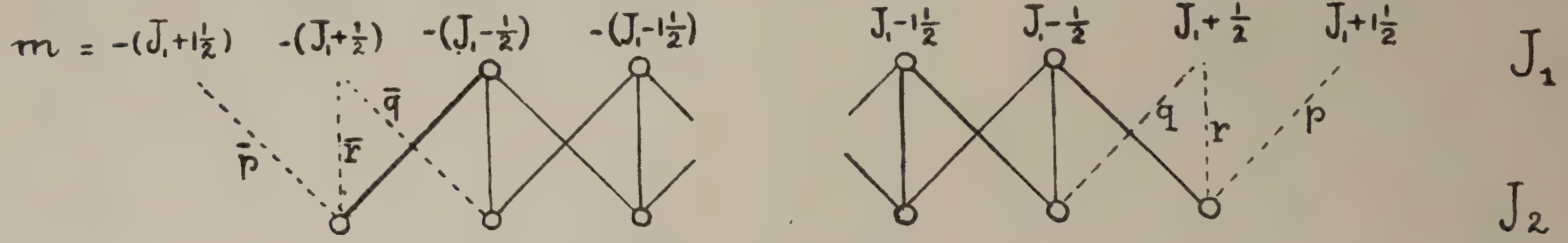


fig. 1 $J_2 = J_1 + 1$

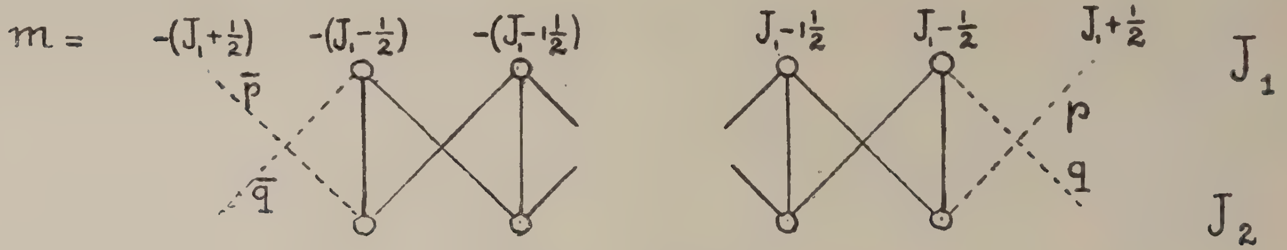


fig. 2 $J_2 = J_1$

The final formulae are therefore:

$$\begin{aligned} i_+ &= \quad A\{m_1^2 + 2(J+1)\,m_1 + (J_1+\tfrac{1}{2})(J_1+1\tfrac{1}{2})\} \\ i_0 &= -4A\{m_1^2 - (J+\tfrac{1}{2})^2\} \\ i_- &= \quad A\{m_1^2 - 2(J+1)\,m_1 + (J_1+\tfrac{1}{2})(J_1+1\tfrac{1}{2})\}. \end{aligned}$$

These formula may also be written symmetrically in the quantum numbers of the initial and final states to bring them in agreement with the formulae (1):

$$J_2 = J_1 + 1 \begin{cases} i_+ = A\,(J_1+\overline{m})\,(J_2+\overline{m}) = A\,(\overline{J}+m_1)\,(\overline{J}+m_2) \\ i_0 = 4\,A\,(\overline{J}^2-\overline{m}^2) \qquad\qquad = 4\,A\,(\overline{J}+\overline{m})\;(\overline{J}-\overline{m}) \\ i_- = A\,(J_1-\overline{m})\,(J^2-\overline{m}) = A\,(\overline{J}+m_1)\,(\overline{J}-m_2) \end{cases}$$

in which $\overline{J}$ and $\overline{m}$ now represent the arithmetical means between the initial and final states. It may also still be shown that these formulae satisfy the condition that the sum of the intensities of the σ-components is equal to that of the π-components.

The same procedure is followed in the case that $J_2 = J_1$. Then according to fig. 2:

$$\begin{aligned} i\,(p) &= -B\{(J_1+\tfrac{1}{2})^2 + \gamma_1\,(J_1+\tfrac{1}{2}) + \gamma_2\} = 0 \\ i\,(\overline{q}) &= -B\{(J_1-\tfrac{1}{2})^2 - \gamma_1\,(J_1-\tfrac{1}{2}) + \gamma_2\} = 0 \end{aligned}$$

from which

$$\underline{\gamma_1 = -1} \qquad \underline{\gamma_2 = -(J_1+\tfrac{1}{2})\,(J-\tfrac{1}{2})}.$$

Likewise

$$\begin{aligned} i\,(q) &= -B\{(J_1-\tfrac{1}{2})^2 + \alpha_1\,(J_1-\tfrac{1}{2}) + \alpha_2\} = 0 \\ i\,(\overline{p}) &= -B\{(J_1+\tfrac{1}{2})^2 - \alpha_1\,(J_1+\tfrac{1}{2}) + \alpha_2\} = 0, \end{aligned}$$

from which

$$\underline{\alpha_1 = 1 = -\gamma_1} \qquad \underline{\alpha_2 = -(J_1+\tfrac{1}{2})\,(J_1-\tfrac{1}{2}) = \gamma_2}.$$

This combined with (5) gives:

$$\underline{\beta_1 = 0.}$$

The simplest way to determine β_2 is now by making use of the fact that in this case for:

$$m_1 = m_2 = 0 \quad , \quad i_0 = 0$$

or, what is more complicated, by requiring the total intensity of the σ-components to be equal to that of the π-components. Then we find:

$$\underline{\beta_2 = 0.}$$

Hence for the case $J_2 = J_1$ the formulae become:

$$\begin{aligned} i_+ &= -B\{m_1^2 + m_1 - (J_1+\tfrac{1}{2})\,(J_1-\tfrac{1}{2})\} \\ i_0 &= 4B\,m_1^2 \\ i_- &= -B\{m_1^2 - m_1 - (J_1+\tfrac{1}{2})\,(J_1-\tfrac{1}{2})\} \end{aligned}$$

or written symmetrically:

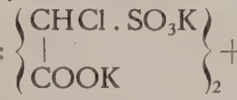
$$J_2 = J_1 \begin{cases} i_+ = \ B(\overline{J} + \overline{m})(\overline{J} - \overline{m}) \\ i_0 = 4B\,\overline{m^2} \\ i_- = \ B(\overline{J} + \overline{m})(\overline{J} - \overline{m}). \end{cases}$$

In both cases the same results may also be obtained, but in a more lengthy way, by carrying out the calculations with the real components at the edges of the schemes.

Leiden, Instituut voor theoretische Natuurkunde.

Chemistry. — *"On the Pseudo-symmetry of Racemic Potassium Chloro-sulfoacetate."* By Prof. F. M. JAEGER.

(Communicated at the meeting of May 30, 1925).

The crystalform of racemic *potassium-chloro-sulfoacetate*, whose constitution is:  $\left\{\begin{matrix} CHCl\,.\,SO_3K \\ | \\ COOK \end{matrix}\right\}_2 + 3\,H_2O$, has not been well known up till now. RATHKE [1]) concluded from his measurements that the compound must be considered to be tetragonal, while DOELTER [2]) described the substance as possessing rhombic symmetry, as a result of very insufficient data obtained by him with evidently badly developed crystals. These showed a combination of a rhombic bipyramid $\{111\}$ and the basis $\{001\}$; the angle $(1\bar{1}1):(111)$ was found to have values ranging from 85° to 88°, while for the angle $(001):(111)$ values are given oscillating between 68° and 72°.

Prof. BACKER was so kind as to put at my disposal some crystals, which he obtained by slow evaporation from aqueous solutions containing also *potassium bromide*. These beautiful crystals appeared to be perfectly clear and to possess perfectly plane, lustrous faces; moreover they showed optical properties of a very particular character, which invited to closer examination. The results obtained during this investigation are here recorded.

The salt crystallizes most frequently in the shape of thin square plates and sometimes also as thick quadratic crystals which are truncated at two opposite corners (Fig. 1). The faces of these crystals were in all cases highly lustrous; the angular values in separate individuals appeared to be very constant, accurate measurements being therefore possible here.

The symmetry is apparently rhombic-bipyramidal, with a very close approximation to tetragonal symmetry; the geometrical form may, therefore, be safely described as pseudo-tetragonal. This fact, which finds its expression also in the values of the crystal-parameters:

$$a : b : c = 0.9973 : 1 : 2{,}7650$$

explains at the same time the discordant results of the measurements of the earlier observers mentioned above.

Observed forms: $c = \{001\}$, always strongly predominant and highly lustrous; on microscopical observation the faces of this form show a very fine striation parallel to the edge $(001):(101)$.

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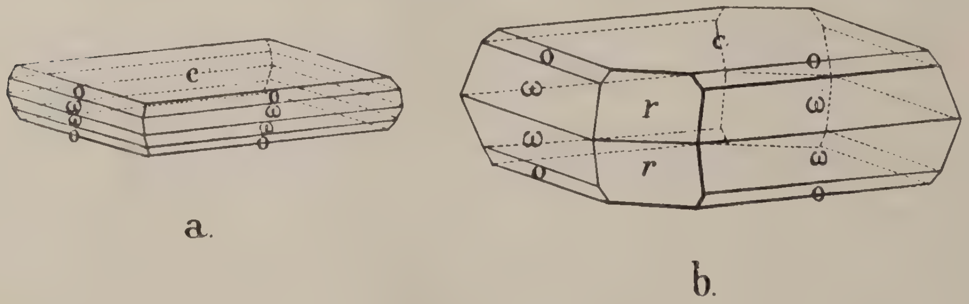
[1]) B. RATHKE, Lieb. Ann. der Chemie, **161**, 166, (1872).

[2]) C. DOELTER, Sitzber. d. Akad. d. Wiss. Wien, **93**, II, 685, (1886); Monatshefte **7**, 159.

Moreover: $\omega = \{111\}$ and $o = \{113\}$, both sometimes equally broad, but in most cases ω appreciably broader than o; the planes of ω give also much better reflections than o, the faces of this latter form being usually finely striated parallel to the edge $(001):(111)$. The bigger and thicker individuals show, moreover, the form $r = \{101\}$, which has also very lustrous faces, yielding very sharp reflexion-images. The plane angles on $\{001\}$ are 89°48′, resp. 90°12′; the faces of $\{001\}$ and in the same way the opposite faces of $\{113\}$ are never completely parallel, but deviate from parallel orientation about 10′.



a.

b.

Fig. 1.

Doubtlessly this fact is connected with the rather complicated structure of the crystals explained in the following.

Angular Values:	*Observed:*	*Calculated:*
$c : \omega = (001) : (111) =$	* 75° 40½′	—
$c : r = (001) : (101) =$	* 70 10½	—
$c : o = (001) : (113) =$	52 34	52° 33′
$o : \omega = (113) : (111) =$	23 6½	23 7½
$\omega : \omega = (111) : (11\bar{1}) =$	28 39	28 39
$o : o = (113 : (\bar{1}13) =$	68 36	68 26
$\omega : \omega = (111) : (1\bar{1}1) =$	86 37	86 18
$\omega : \omega = (111) : (\bar{1}11) =$	86 21	86 41
$o : o = (113) : (1\bar{1}3) =$	68 25	68 10
$r : r = (101) : (10\bar{1}) =$	39 39	39 39

The crystals show a good cleavage parallel to $\{001\}$.

Optical Properties.

In parallel polarized light the crystals show diagonal extinction on $\{001\}$. However, they clearly possess a zonal structure: generally there is a central, quadratically limited field, which is divided into four quadrants separated by boundary-lines parallel and perpendicular to the edge $c:r$. The pairs of opposed quadrants have always the same optical orientation. Round this central part succesive zones are arranged,

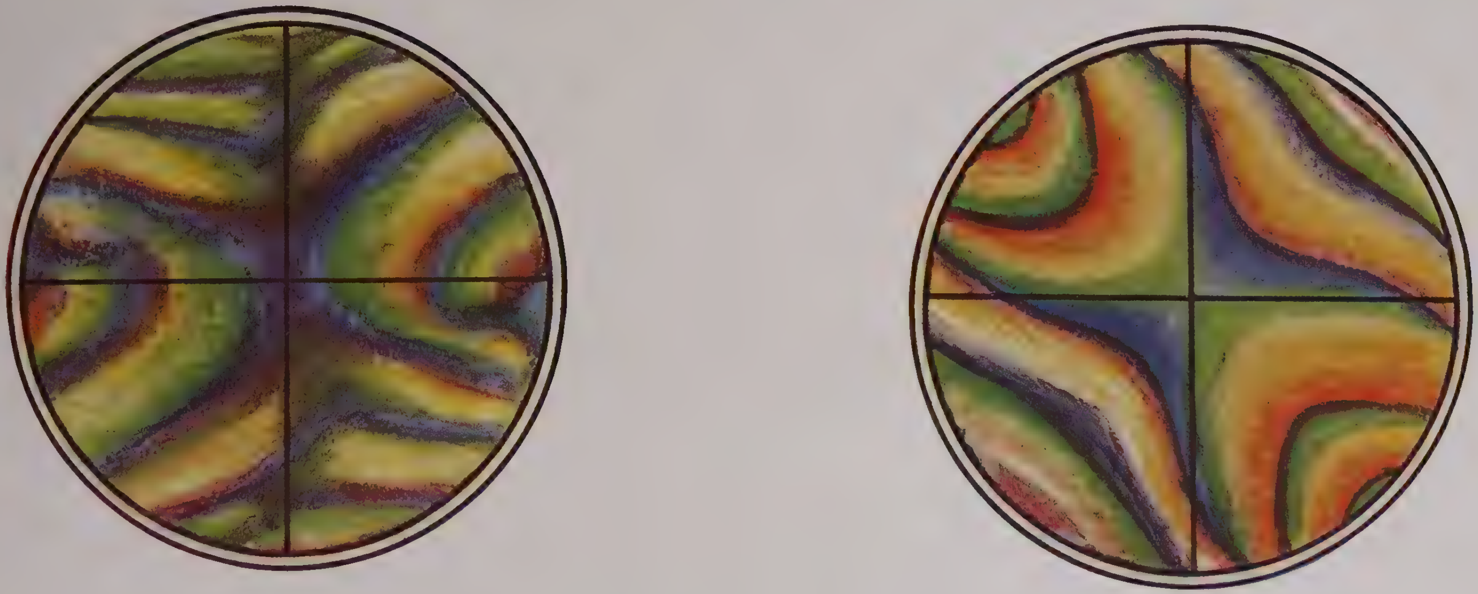


Fig. 2

a.

Normal Position

(Axial plane horizontally orientated)

b.

Diagonal Position

RACEMIC POTASSIUM-CHLOROSULFOACETATE

which go parallel to the boundaries of the square plates; these zonal bands appear to get thinner, as they approach the circumference of the crystal-plates. The plane of the optical axis for yellow light in each band is parallel to $\{100\}$; the direction of the *c*-axis is that of the first bisector, with negative optical character.

In convergent polarized light one observes a strangely shaped interference-image (Fig 2^a), if the principal sections of the Nicol's prism are parallel to the diagonals of (001). When the crystal is turned over 45°, the interference-image is that represented in Fig. 2^b; there are no branches of a dark hyperbola present. The axial image of Fig, 2^a is evidently only *centrically*-symmetrical: it shows an extremely strong *crossed* dispersion of monoclinic character, with $\varrho < v$.

From this it follows that the structure is only rhombic in appearance; in reality it is monoclinic. By an almost perpendicular crossing of monoclinic lamellae a polysynthetic twin-structure is created, which very closely imitates a pseudo-rhombic, and almost tetragonal regularity. To this intergrowth of monoclinic lamellae correspond as well the fine striations on the faces of $\{001\}$ and $\{113\}$, as the irregularities of the architecture of the crystals, as they are revealed by the more significant oscillations of the angular values in the zone of the edge $(001):(101)$ caused by the want of parallelism between (001) and $(00\bar{1})$. It was impossible to intensify the lamellar appearance of the crystals by heating, because the crystals on heating very soon show numerous bursts and then get turbid and opaque by deshydration.

The pseudo-symmetrical character of the crystals thus being established beyond all doubt, suspicion arises that the salt is no racemate in the proper sense of the word, but rather a pseudo-racemic intergrowth of 50 $^0/_0$ of the right- and lefthanded antipodes. Certainty about this could only be obtained, if it were possible to compare the crystalforms of the optically active components separately with that of the salt described. However, this experiment remains irrealisable as a consequence of the fact that the potassium-salts of the optically-active chloro-sulfoacetic acids are very rapidly racemized in solution, it being, therefore, impossible to get measurable crystals of both components in a pure state.

Laboratory for Inorganic and
Physical Chemistry of the University.

Groningen, (Netherlands), May. 1925.

Botany. — *„Ueber die Gültigkeit des Sinusgesetzes für die geotropische Reizung von Avena-Koleoptilen bei kleinen Ablenkungswinklen."* Von Dr. ERICH SCHNEIDER. (Communicated by Prof. F. A. F. C. WENT.)

(Communicated at the meeting of June 27, 1925).

Die Untersuchungen von RUTTEN—PEKELHARING über die Perzeption des Schwerkraftreizes [1]) haben bewiesen, dass für die geotropische Reizung von Koleoptilen von *Avena sativa* und Wurzeln von *Lepidium sativum* das Produktgesetz (Reizintensität × Reizdauer = konstant) Gültigkeit hat, wenn die Neigung, bei der die geotropische Reizung erfolgt, eine nicht zu geringe Ablenkung von der Vertikalen bedeutet, d.h. die Neigungswinkel nicht unter etwa 20° oder über 170° gross waren.

Es schien wahrscheinlich, dass diese Abweichungen, die sich bei der Reizung bei kleinen Ablenkungswinkeln gezeigt hatten, sich als Versuchsfehler herausstellen dürften, wenn es gelänge, die Untersuchungsmethoden entsprechend zu verfeinern.

Durch Vermittlung von Herrn Professor KÜSTER, dem ich hierfür auch an dieser Stelle Dank sagen darf, hatte ich Gelegenheit, in den Monaten März und April 1925 am botanischen Laboratorium der Universität Utrecht Untersuchungen über die angeregte Frage anzustellen. Meine Aufgabe bestand darin, zu prüfen, inwieweit sich mit den inzwischen sehr verfeinerten Methoden die Gültigkeit des Produktgesetzes für Avenakoleoptilen für die geotropische Reizung bei kleinen Ablenkungswinkeln ebenso befriedigend bestätigen liesse, wie es bei Wurzeln von *Lepidium sativum* schon RUTTEN—PEKELHARING [2]) und später auch TRÖNDLE [3]) gelungen war, der mit genaueren Methoden arbeiten konnte.

Den Gültigkeitsnachweis für das Produktgesetz bei kleinen Ablenkungswinkeln versuchte ich durch Bestimmung der Präsentationszeit bei den verschiedenen Neigungswinkeln zu erbringen und durch die Nachprüfung, inwieweit die gefundenen Präsentationszeiten mit den errechneten übereinstimmten. Grundlage für die Berechnung der Präsentationszeiten war die von mir in zahlreichen Versuchen ermittelte Präsentationszeit für 90° Ablenkung. Betrug diese x Sekunden, so errechnete sich die Präsentationszeit für andere Winkel hieraus durch Multiplikation von x mit dem Sinus des Ablenkungswinkels a (Präsentationszeit $= x \; sin. a$).

Die Methode nach der ich meine Versuche anstellte war die folgende: Zu den Versuchen wurden Früchte der reinen Linie „Siegeshafer" verwandt, die nachdem sie von den Spelzen befreit worden waren, bei 24° C. auf feuchtem Filtrierpapier zum Keimen ausgelegt wurden. Nach zwei Tagen wurden die Keimlinge in einer Reihe in längliche Zinkkästchen (20/3/3 cm.) voll feuchter Erde eingepflanzt, ca. 12 Pflanzen in jedes Kästchen. Die Kästchen mit den Keimlingen blieben im Dunklen bei ca. 25—26° C. 36 Stunden stehen und wurden dann, gerade wenn die Spitzen der Koleoptilen über der Erde sichtbar wurden, in das Dunkelzimmer mit konstanter Temperatur gebracht, in dem die Versuche vorgenommen werden sollten. Das Ueberführen der Versuchspflanzen in das Zimmer mit konstanter Temperatur geschah in lichtdicht verschlossenen Kästen. Wenn die Koleoptilen eine Länge von wenigstens 1.5 cm. über der Erde erreicht hatten, was weitere 24 Stunden dauerte, wurden die Pflanzen zu den Versuchen verwendet.

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[1]) RUTTEN—PEKELHARING, C. J.: Untersuchungen über die Perzeption des Schwerkraftreizes (Rec. d. trav. bot. Néerl. **7**, 1910, 241).

[2]) RUTTEN—PEKELHARING: a. a. O., 278.

[3]) TRÖNDLE, A.: Untersuchungen über das Sinusgesetz bei den geotropischen Reaktionen von *Lepidium* (Jahrb. f. wiss. Bot. **60**, 1921, 295).

Da schon beim Auslegen der Haferkörner zum Keimen darauf geachtet wurde, dass nur gleich grosse Körner Verwendung fanden, und da beim Einpflanzen der Keimlinge nur solche benützt wurden, die in gleicher Zeit gleich gross geworden waren, gelang es bald, gleichmässiges und regelmässig gewachsenes Pflanzenmaterial für die Versuche zu erhalten. Waren in einem der Zinkkästchen einige Pflanzen nicht ganz gerade, so wurden sie vor dem Versuch entfernt.

Die Versuche selbst wurden im Dunkelzimmer bei konstanter Temperatur (20 C.) angestellt. Die relative Feuchtigkeit des Zimmers liess sich durch ein ständig beriesseltes Tuch nahezu konstant halten (60—63 %). Schwankend war nur die Feuchtigkeit der Erde in den Zinkkästchen, da diese täglich begossen werden mussten.

Die Koleoptilen wurden gereizt, indem die bepflanzten Zinkkästchen auf einem Brett befestigt wurden, das sich um bestimmte, an einer Skala abzulesende Winkel neigen liess, ähnlich dem von RUTTEN—PEKELHARING benutzten Apparat [1]). Nach der Reizung wurden die Kästchen auf den HARREVELD'schen Klinostaten [2]) übertragen und rotierten um die horizontale Klinostatenachse. Mit der Notwendigkeit des Uebertragens der Versuchspflanzen vom Kippbrett auf den Teller des Klinostaten war jedoch eine Fehlerquelle gegeben (Erschütterung, Unmöglichkeit genauer Horizontallage des Kästchens während des Transportes) die wohl bei Verwendung grosser Neigungswinkel unberücksichtigt bleiben konnte, bei Ablenkungswinkeln von 10° und weniger jedoch sichtlich zu Ungenauigkeiten führte. Daher wurde bei solchen und zur Kontrolle auch wiederholt bei grösseren Neigungswinkeln eine andere Versuchsanordnung gewählt. Die Reizung erfolgte auf dem Teller des Klinostaten selber. Der Teller des von mir für diesen Zweck benutzten Klinostaten nach DE BOUTER [3]) konnte in jede Neigung zur Vertikalen gebracht und in dieser Lage befestigt werden.

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[1]) RUTTEN—PEKELHARING: a. a. O., 255.

[2]) HARREVELD, PH. VAN: Ein Universalklinostat (Rec. d. trav. bot. Néerl. **9**, 1912, 170).

[3]) WENT, F. A. F. C.: On a new clinostat after DE BOUTER (Proc. Akad. Amsterdam **25**, 1922, 475).

Nach der Reizung wurde die Klinostatenachse horizontal gestellt; gleichzeitig begann die Rotation des Klinostatentellers, sodass zwischen dem Ende der Reizung und dem Beginn der Rotation weniger als eine Sekunde verstrich und Erschütterungen der Versuchspflanzen nahezu vermieden waren.

Die Reaktionszeit schwankte zwischen 30 und 35 Minuten. Als Reaktionszeit betrachtete ich die Zeit, die zwischen dem Ende der Reizzeit und dem Zeitpunkt verstrich, bei dem 50 % der überhaupt auftretenden Krümmungen eingetreten waren. Die Ablesung des Versuchsergebnisses erfolgte jedoch erst, wenn alle überhaupt eintretenden Krümmungen sichtbar waren, also nach einer längeren Zeitspanne nach Ablauf der Reizzeit als die Reaktionszeit angibt. Der Zeitpunkt der Ablesung lag ca. 40 Minuten nach Schluss der Reizung. Nach weiteren 10 Minuten (50 Minuten nach Ablauf der Reizzeit) wurden bereits einige Krümmungen wieder undeutlich.

Als Präsentationszeit wurde die Zeit betrachtet, für deren Dauer die Versuchspflanzen gereizt werden mussten, sodass 50 % der Koleoptilen sich negativ geotropisch krümmten.

Bei der Entscheidung der Frage, ob eine Koleoptile als gekrümmt oder ungekrümmt zu betrachten ist, wird es sich nicht vermeiden lassen, eine willkürliche Grenze zu wählen, die für alle Versuche gültig zu bleiben hat. Ich habe stets Koleoptilen, die keine Krümmung, wohl aber einen deutlich monosymetrischen Vegetationspunkt hatten, als ungekrümmt notiert (Siehe hierzu auch die Abb. von gekrümmten und deformierten Wurzelspitzen der Lupine bei Riss [1]).

Es wurde zunächst die Präsentationszeit für 90° Ablenkung bestimmt, die als Grundlage zur Berechnung für die anderen Neigungswinkel dienen sollte. Sie wurde aus 45 Versuchen mit insgesammt etwa 800 Versuchspflanzen ermittelt und betrug 202 Sekunden. Die von mir gefundene Präsentationszeit ist beträchtlich kürzer als die von Rutten—Pekelharing [2]) für *Avena*-Koleoptile ermittelte (269 Sekunden bei 24° C., also für 20° C. noch länger).

Nachdem die Präsentationszeit für 90° Ablenkung gefunden war, wurde diese auch für 60°, 45° und 30° Neigung bestimmt. Es war zuerst meine Absicht, die Präsentationszeiten für diese Winkel experimentell zu finden und dann zu prüfen, ob der gefundene Wert mit dem erst dann errechneten übereinstimmte. Diese Arbeitsweise war jedoch so zeitraubend, dass ich sie nur für den Ablenkungswinkel 45° anwandte: Präsentationszeit = 285 Sekunden. Für die weiteren Winkel verfuhr ich in der Weise, dass ich prüfte, ob die nach dem Sinusgesetz errechnete Präsentationszeit sich durch das Experiment als richtig erwiess. Das war der Fall; die errechneten Präsentationszeiten für:

60°	233 Sekunden
30°	403 Sekunden

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[1]) Riss, M. M.: Ueber den Einfluss allseitig und in der Längsrichtung wirkender Schwerkraft auf Wurzeln (Jahr. f. wiss. Bot. **53**, 1914, 162).

[2]) Rutten—Pekelharing: a. a. O., 268

zeigten sich experimentell als zutreffend: Wurden *Avena*-Koleoptilen bei den verschiedenen Ablenkungswinkeln solange gereizt, als die zugehörigen Präsentationszeiten angaben, so krümmten sich 50 % der Versuchspflanzen negativ geotropisch.

Die Bestimmung der Präsentationszeit für 45° Ablenkung erfolgte in 25 Versuchen mit insgesamt 426 Versuchspflanzen. Zur Nachprüfung der errechneten Präsentationszeiten für 60° und 30° wurden je 10 Versuche angestellt mit durchschnittlich je 20 Versuchspflanzen.

Die errechnete Präsentationszeit für 10° Ablenkung (1155 Sekunden) wurde sowohl durch Versuche auf dem Kippbrett und Uebertragen der gereizten Pflanzen auf den Teller des HARREVELD'schen Klinostaten nachgeprüft als auch durch solche, die unter Vermeidung des Uebertragens auf dem Klinostaten nach DE BOUTER vorgenommen wurden. Beide Methoden ergaben befriedigende Resultate: im Durchschnitt waren 50 % der Koleoptilen gekrümmt.

Bei einer Ablenkung von 5° konnten nur noch auf dem kippbaren Teller des DE BOUTER'schen Klinostaten eindeutige Resultate erzielt werden. Die errechnete Präsentationszeit (2312 Sekunden) wurde durch 25 Versuche mit zusammen ca. 500 Pflanzen bestätigt.

Um eine Kontrolle darüber zu haben, inwieweit eine Abweichung von der Präsentationszeit Anlass zu Schwankungen des Prozentsatzes der Krümmungen gäbe, wurden Versuche angestellt, bei denen die Koleoptilen von *Avena* etwas länger oder weniger lang gereizt wurden, als die errechnete und empirisch gefundene Präsentationszeit angab. Dabei stellte sich heraus, dass bei den grossen Neigungswinkeln (Winkel gegen 90°) schon eine sehr geringe Abweichung von der Präsentationszeit einen anderen Prozentsatz von gekrümmten Koleoptilen ergab als den bei Reizung für die Dauer der Präsentationszeit beobachteten. Die errechnete Präsentationszeit für 80° Ablenkung (205 Sekunden) ergab auch wirklich 50 % Krümmungen. Wie die nebenstehende Tabelle zeigt, krümmten sich bereits weniger als 50 % der Koleoptilen, wenn bei 80° Neigung 3 Sekunden kürzer, als die Präsentationszeit betrug, gereizt wurde, nämlich für die Dauer der Präsentationszeit von 90° = 202 Sekunden.

Nr.	Dat.	Zeit	Ablenk.	Reizz.	Reaktz.	Länge d. Koleoptilen	Zahl	Gekrümmt	Ungekr.	%
115	18.4	6^{00}	90°	202 Sek.	34 Min.	1,5—2,5 cm.	16	8	8	50%
120	18.4	8^{00}	80°	202 Sek.	35 Min.	1,75—2,5 cm.	18	8	10	45%
90	1.4	11^{30}	80°	205 Sek.	35 Min.	1,5—2,5 cm.	24	12	12	50%

Bei den Versuchen wurden bisweilen Störungen beobachtet, die zu erklären mir nicht gelungen ist. Da diesen Störungen gewisse Gesetzmässigkeiten zu Grunde liegen, scheint es angezeigt, über sie zu berichten.

An manchen Tagen war bei den *Avena*-Koleoptilen die Präsentationszeit für die verschiedenen Ablenkungswinkel eine geringere, sodass bei Reizung in der Dauer der oben angegebenen Präsentationszeiten mehr als 50 % gekrümmte Koleoptilen beobachtet wurden.

So lieferte z. B. am 20. März bei den Ablenkungswinkeln 5°, 45°, 80° die Reizung für die Dauer der Präsentationszeit 75 %, 78 %, 80 % und 70 % gekrümmte Koleoptilen. Diese Tatsache zwang mich, an allen Tagen vor Beginn der Versuche bei den verschiedenen Ablenkungswinkeln stets erst nachzuprüfen, ob bei 90° Ablenkung die Reizung für die Dauer der Präsentationszeit (20 Sekunden) auch wirklich 50 % gekrümmte Koleoptilen lieferte. Erst wenn das der Fall war, konnten weitere Versuche vorgenommen werden.

Auffällig ist, dass an solchen Tagen grösserer Reizempfindlichkeit eine grössere Anzahl Pflanzen als sonst aus dem zu den Versuchen zu verwendenden Material ausgeschaltet werden musste, da ihre Koleoptilen nicht ganz gerade waren. Die Ursache für die Schwankung der Reizempfindlichkeit der *Avena*-Koleoptilen habe ich nicht ermitteln können.

Von grosser Wichtigkeit ist es, für alle Versuche Koleoptilen gleicher Länge zu verwenden (1.5—2.5 cm.). Kürzere Koleoptilen sind weniger reizempfindlich. 1 cm. lange Koleoptilen gaben bei 60° und 233 Sekunden (= Präsentationszeit) nur 34 % Krümmungen. Auch für lange Koleoptilen verlängern sich die Präsentationszeiten, ganz abgesehen davon, dass solche Koleoptilen sich schon deshalb nicht zu den Versuchen eignen, weil sie selten so durchaus gerade sind und senkrecht stehen, wie das unbedingt notwendig ist.

Zusammenfassend komme ich zu der Feststellung, dass für die geotropische Reizung von *Avena*-Koleoptilen das Produktgesetz, da es sich auch bei kleinen Winkeln als zutreffend erwiess, uneingeschränkte Gültigkeit hat. Diese Tatsache steht im Gegensatz zu der Ansicht RISS's [1]), nach welcher das Sinusgesetz für diesen Fall keine Gültigkeit beanspruchen kann.

Die Reizempfindlichkeit der *Avena*-Koleoptilen ist an gewissen Tagen eine erhöhte. Sie schwankt auch mit der Länge der Koleoptilen: Kurze Koleoptilen (1 cm. und weniger) sind weniger reizempfindlich als solche von 1.5—2.5 cm. Länge.

Erst nach Abschluss des Manuskriptes ist mir die Arbeit von BREMEKAMP in den Berichten der D. botan. Gesellschaft (*43*, 1925, 159.) zugänglich geworden. Die von BREMEKAMP untersuchte Dorsiventralitätskrümmung der Koleoptilen kann bei meinen Versuchen keine Fehler verursacht haben, da die Keimlinge immer in der gleichen Richtung in die Zinkkästchen gepflanzt wurden, und zwar so, dass die Längsachse der keimenden Haferfrüchte parallel zu den schmalen Wänden des Kästchens zu liegen kam. Falls Dorsiventralitätskrümmungen auftraten, so mussten diese demnach in einer Ebene erfolgen, die senkrecht stand zu der Ebene, in der die von mir zu beobachtenden Krümmungen lagen, und können so bei der Ablesung des Versuchsergebnisses nicht zu Irrtümern Anlass gegeben haben.

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[1]) RISS; a. a. O., 208.

Zum Schlusse möchte ich Herrn Professor WENT, der die Anregung zu der hier beschriebenen Untersuchung gab, es ermöglichte, sie an seinem Laboratorium auszuführen, und mir zu diesem Zwecke alle Hilfsmittel seines Institutes zur Verfügung stellte, ebensosehr hierfür danken wie für das stete Interesse, das er meinen Versuchen entgegenbrachte.

Giessen, im Mai 1925.

Anatomy. — *"The myelencephalic gland of Polyodon, Acipenser and Amia"*. By Dr. C. J. VAN DER HORST. (Central Institute of Brain Research, Amsterdam). (Communicated by Dr. C. U. ARIËNS KAPPERS.)

(Communicated at the meeting of April 25, 1925).

When dissecting the brain of Polyodon I found a darkly pigmented, lozengeshaped mass surrounding the foremost part of the spinal cord closely behind the calamus scriptorius. This structure encircles the spinal cord very closely. At the dorsal side it reaches somewhat further caudad than at the ventral side. I prepared this mass with the brain out of the skull and have cut it in serial sections which are stained in different ways. While examining this mass, it appeared to be a bloodgland, the histological structure of which will be discussed closer in this paper.

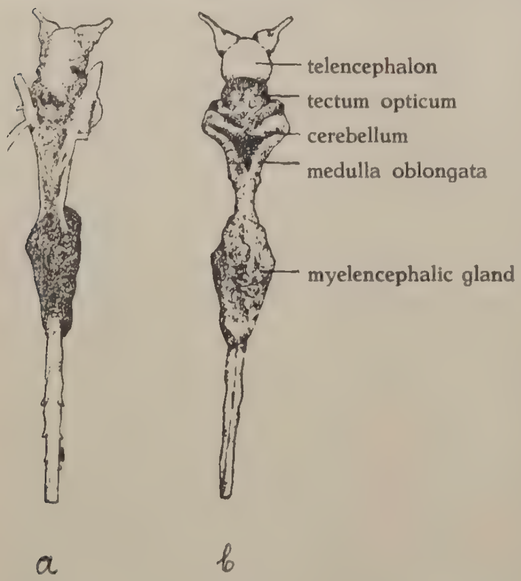

Fig. 1. Brain and frontal part of the spinal cord of Polyodon. *a* ventral, *b* dorsal.

In literature a similar gland is only known in Lepidosteus, where it has been accurately described and figured by CHANDLER. In this fish the gland covers a part of the medulla oblongata, being situated a little more frontally than in Polyodon. CHANDLER calls it "myelencephalic gland", a name which I wish to obtain here, though the gland is situated quite behind the myelencephalon in Polyodon. As this gland immediately strikes us while dissecting the brain, this somewhat more caudal situation can not be the reason that CHANDLER did not find it in Polyodon, no more than in Amia, where it is also very large and even situated on the myelencephalon, and in Acipenser, where the gland is to be found partly in front of and partly behind the calamus scriptorius. CHANDLER himself admits the possibility that the gland was removed together with the perimeningial tissue in the brains of the fishes, examined by him. This must have been indeed the case. In Polypterus, however, I could not find the gland though it certainly should still be present in the specimen dissected by me, if it had been there.

Neither could I find it in Megalops or in other teleosts. CHANDLER suggests the possibility, but not the probability, that the saccus endolymphaticus which covers the fourth ventricle in Protopterus according to BURCKHARDT may be related in some way to the bloodgland of Lepidosteus. Besides that here this is a real saccus endolymphaticus, so a part of the internal ear, this organ of Protopterus has quite a different microscopical structure than the myelencephalic gland of Lepidosteus, so that in my opinion all relation must be excluded. So this gland is found as a well defined structure only in Lepidosteus and Amia, Polyodon and Acipenser.

MOODIE described fossil fish brains from the coal measures of Kansas. In all probability these are brains of representatives of the Palaeoniscidae, a family related to the recent sturgeons. In these brains closely behind the calamus scriptorius a large eminence is found. MOODIE supposes this eminence to be an unpaired vagal lobe. But as such large vagal lobes are found only in Cyprinidae and Siluridae among recent fishes and not at all in Chondrostei, I think it very probable that this structure is also a myelencephalic gland.

In Amia the myelencephalic gland has the shape of a triangular mass that covers the fourth ventricle and the foremost part of the spinal cord. The apex of this triangle is turned to the front and reaches the caudal side of the cerebellum. At the base of the triangle the gland surrounds the spinal cord in a wide curve. According to my opinion the wideness of this curve cannot only be ascribed to shrinkage. There must be a good distance between the glandular tissue and the spinal cord in Amia, which is not the case in Polyodon and Acipenser. Behind the vagal root the gland is connected with a mass in the shape of a long quadrangle that reaches at the ventral side as far frontal as is the case with the gland at the dorsal side. The earlike lobes, described by CHANDLER in Lepidosteus, are lacking in Amia as well as in Polyodon and Acipenser.

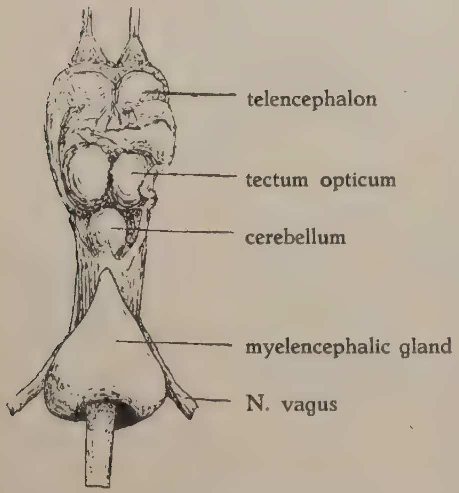

Fig. 2. Brain with myelencephalic gland of Amia.

In a young specimen of Acipenser ruthenus I found the myelencephalic gland near the calamus scriptorius. When seen from the dorsal side it has the same shape as the gland in Polyodon, but at the ventral side of the spinal cord the glandular tissue is not present, so that the gland is crescentic in cross section. In a very large specimen of Acipenser sturio a large mass of fat is found at the same place. So it is probable that the gland in Acipenser degenerates in older animals. This is certainly not the case in

Amia, because the specimens, examined by me, were adult ones. Of Polyodon I possessed only young specimens of about 20 to 25 cm. total length. So I can not find out, if the gland in Polyodon also becomes degenerated at higher age.

At the microscopical examination the gland appears to be situated in the perimeningial tissue wholly external to the meninx primitiva. Whereas in Amia there is a great space between the meninx primitiva and the glandular tissue, in Polyodon the gland immediately touches the meninx and in cross section it extends from the meninx to the perichondrium (fig. 6).

The microscopical structure of the myelencephalic gland is very much like that of the spleen. The glandular tissue itself consists of rather large polygonal cells. They have a large nucleus which may be simply round, but in general it is oval or of an irregular shape (fig. 3). Often it is curved, sometimes S-shaped, sometimes the nucleus may consist of some pieces, which, nearly without mutual connection, lie scattered in the protoplasm. In this respect, as also in size, reaction to dyes and structure of the protoplasma and the nucleus these cells quite agree with the leucocytes, which are found numerously in the bloodvessels. I think I have the right

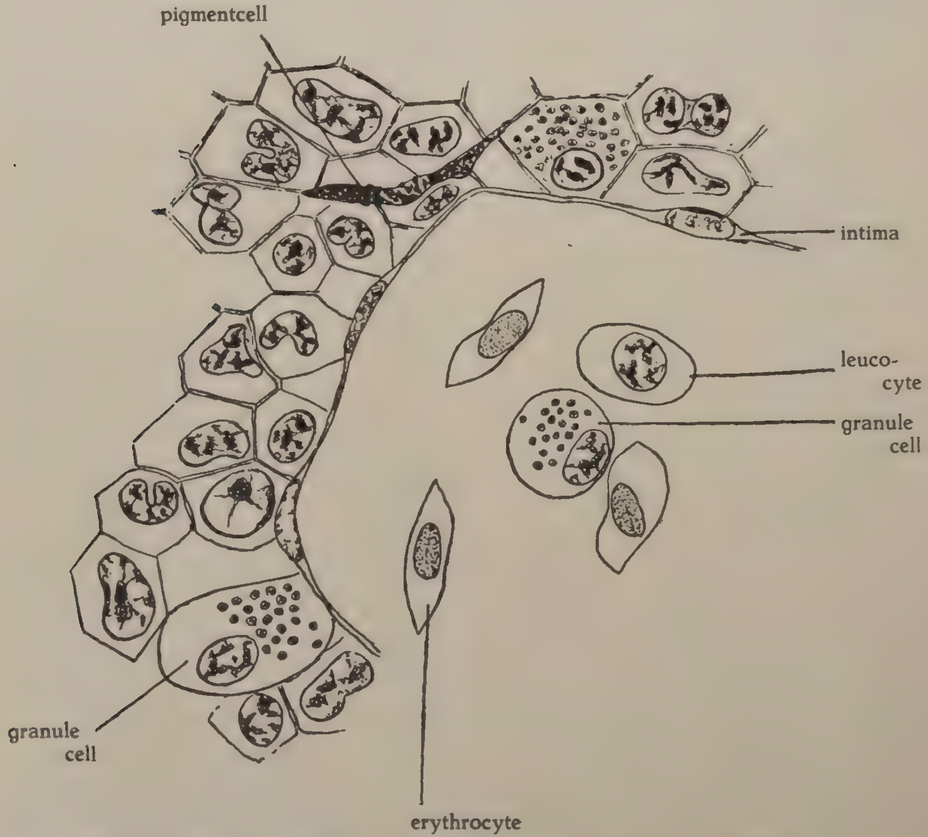

Fig. 3. Tissue and bloodsinus of the myelencephalic gland of Polyodon.

to suppose that these cells are young leucocytes which find their origin here, though I did not find mitoses. But often these cells can be seen projecting partly in a vessel.

In this tissue, cells are scattered with a more regular nucleus, which strike us by a great number of granules in the protoplasma. Some are not or hardly larger than the leucocytes, but most of them are up to twice as large. These same cells are found in certainly the same if not in greater number in the bloodvessels, also I found some projecting partly in a vessel. The number of granules in these cells varies very much. In general the small ones have few granules, the larger ones possess more, some are wholly filled with granules. These granules are strongly stained with haematoxyline, so that contrastaining with eosine had no result. Especially in Weigert-preparations these cells are very obvious, the granules being stained intensely black by this method. My material does not allow me to examine, whether we have before us oxyphil or eosinophil leucocytes with coarse granules or basiphil mastcells. According to CHANDLER the granular cells are intensively stained with eosine, KAPPERS found them stained with picrid acid. On the other hand SUNDWALL mentions that the granular cells occurring in other animals in similar places which will be discussed later on show a decided affinity to basic deyes.

According to Miss SABIN, who described the development of the different bloodcells in the chicken, the granulocytes have no relation whatsoever to the endothelial cells. Also Miss DANTSCHAKOFF has demonstrated that the granulocytes are extravascular from origin. I found this confirmed in Polyodon. All endothelial cells have a much smaller nucleus than the leucocytes or the granulocytes. But these two latter ones are closely related to each other. As has already been said before, the granulocytes with few granules are not larger than the leucocytes and the presence or the lacking of these few granules in that case is the only difference between these cells.

In this tissue a venous network of capillaries and sinusses is found, almost quite filled with erythrocytes. These erythrocytes are oval in shape, like in all lower vertebrates, and seen from the side they are spindleshaped, showing often a slight depression in the centre (fig. 3). They have a rather small oval nucleus, in which the chromatine is regularly distributed. In this respect they can be distinguished at once from the leucocytes, in which the chromatine is irregularly distributed. According to CHANDLER the erythrocytes are scattered freely throughout the gland, entirely independent of vessels of any sort. I could not find this in my preparations, the erythrocytes being found only in the bloodvessels. Also I think it probable that the cells, called erythrocytes by CHANDLER, are not erythrocytes, as they quite deviate from the characteristic form of these cells in other animals.

The bloodsinusses are only bordered by a well defined intima, consisting of very flat endothelial cells with oval nuclei, so they have quite the character of perimeningial bloodsinusses. In the larger sinusses the intima is continuous (fig. 3). But in the smaller ones interruptions seem to occur in the intima. This is certainly the case, where leucocytes or granulocytes protrude in the vessels.

At the periphery the gland is more compact and the capillaries cross it in all directions, but they are few in number compared with the amount of glandular tissue. In the midst of the gland and at the dorsal side of the spinal cord, however, the number of capillaries is much more numerous. Also these capillaries run in fronto-caudal direction for the greater part. The glandular tissue between them is reduced to columns with a breadth of a few cells.

At the caudal side and dorsal to the spinal cord the glandular tissue passes in a tissue which seems to be adipose tissue. At least in the celloidine sections this tissue proves to consist of a great number of round cavities with protoplasma and some nuclei between them ; cellmembranes could not be discerned here (fig. 4). This same tissue was found also at the frontal side of the gland, but here ventrally to the spinal cord. In paraffine sections this tissue is greatly deformed and lookes like a reticular mass. CHANDLER describes it as such in Lepidosteus. However, with this difference that the reticular network is found here scattered everywhere between the glandular tissue, so that CHANDLER supposes it to be a framework for the entire structure. In this tissue the bloodvessels of the gland collect in some sinusses, which are situated, for the greater part at least, frontally at the ventral and caudally at the dorsal side of the spinal cord.

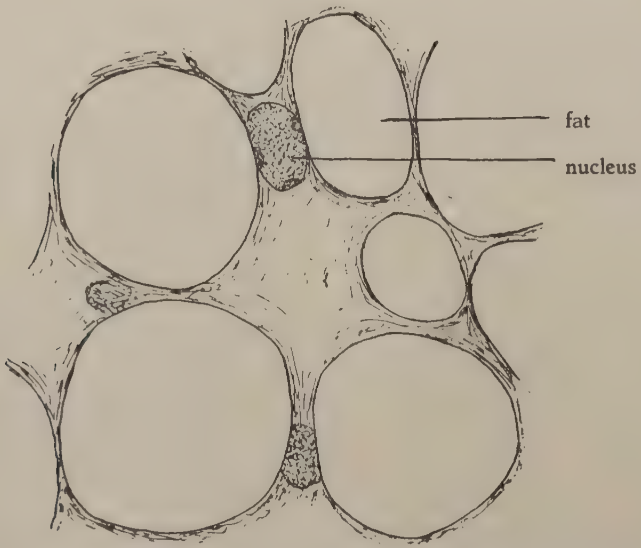

Fig. 4. Adipose tissue near the myelencephalic gland of Polyodon.

In Amia the triangular structure covering the oblongata also consists of similar glandular tissue. As has been said before, in this animal the gland is connected behind the vagus root with a mass of tissue, situated at the ventral side of the oblongata. In the parts connecting the dorsal and ventral masses the glandular tissue is substituted gradually by the reticular connective tissue. Probably this is also of an adipose character, though I can not say this with certainty. This tissue is very obvious in Amia by the great number of veins, so that the whole mass ventral of the oblongata has a somewhat red color. The dorsal side of the gland itself in Amia is covered also by a thin layer of the reticular tissue, whereas in Polyodon the glandular tissue is in direct contact with the perichondrium of the vertebral canal.

A very striking element of the gland and of the surrounding tissue are large, profusely branched pigmentcells. In Polyodon they are especially striking, the gland being nearly wholly black. In Amia I found less of these cells and they are much smaller than the pigmentcells in the membranes that cover the midbrain and the cerebellum. According to CHANDLER these pigmentcells send their branches freely in all directions between the glandular tissue in Lepidosteus. In Polyodon, however, I found these black pigmentcells in a dense layer immediately below the surface of the gland, where they arborize principally parallel to the surface, so that in cross sections they look like lines and are seen only in their real shape in the first sections that touch the gland, there where the surface of the gland is almost in the plane of the sections (fig. 5). Between the glandular tissue only a few of these cells are situated and these are scattered and send their

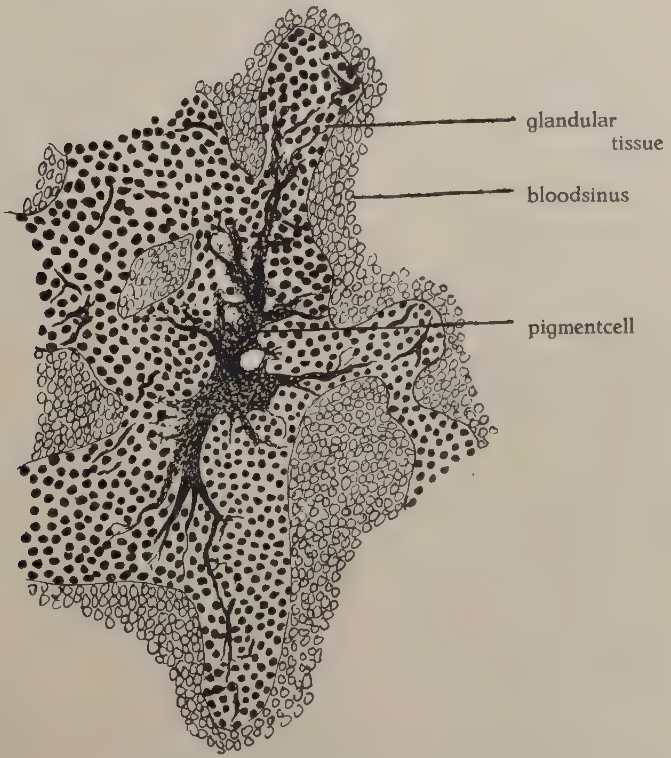

Fig. 5. Pigmentcell in the myelencephalic gland of Polyodon.

branches in all directions. However, they increase in number again around the spinal cord, where they arborize again parallel the surface of the spinal cord. In the connective tissue frontal and caudal to the gland only few of these pigmentcells are situated except at the surface of the large bloodsinusses in this tissue, where there are many.

Concerning the bloodsupply of the gland I observed the following in Polyodon: Where the carotis interna reaches the brain near the infundibulum, it sends a large branch in caudal direction, the arteria encephalica posterior, described by STERZI in selachians. The right and the left artery run together in the perimeningeal tissue at the ventral side of the midbrain and the medulla oblongata in caudal direction, giving off again and again larger or smaller branches which penetrate into the brainsubstance. In the most caudal part of the oblongata I twice found an anastomosis of the right and the left artery; a total union to an arteria basilaris, however, as has been described by STERZI in selachians, does not exist here. But taking in account the more caudal relations, the right artery may be compared with the arteria basilaris. Later on the left artery splits up in two branches. One branch runs along the left to the dorsal side of the spinal cord and seems to serve principally for the bloodsupply of the spinal cord. The other branch curves in ventral direction and runs there caudad at a great distance from the spinal cord but still situated in the perimeningeal tissue. In the frontal part of the gland this artery approaches the spinal cord again, but here it is much smaller, so in this way it is not excluded that small sidebranches have been given off, though I could not find them. I will go on to call this artery the left one, just as the other the right one, though these names are suitable only in respect to the situation of the arteries in front of the gland. In the gland itself these names are not properly suitable, as we will see. In the mean time also the right artery has given off a sidebranch that runs along the right side of the spinal cord in dorsal direction, while the right artery itself goes on in caudal direction. Soon it splits in two equal parts, one of which runs approximately straightly caudad, while the other part curves in ventral direction but soon approaches again the spinal cord, where both parts of the right artery continue in caudal direction symmetrically situated, in the same way as happens with the right and the left artery below the medulla oblongata. In this respect the right artery corresponds to the arteria basilaris of selachians that splits also in two vessels running parallel to each other. In the foremost part of the gland these two arteries approach the spinal cord more and more, so that finally they are taken up in the meninx primitiva, which is much thickened here at the ventral side (fig. 6). In this thickened part of the meninx also the left artery penetrates running here in caudal direction between the two other arteries. The two parts of the right artery remain in the meninx primitiva and seem to serve mainly for the bloodsupply of that part of the spinal cord, that is surrounded by the gland. Gradually they diminish in size and at the caudal end of the gland they have almost disappeared. The left artery leaves the meninx primitiva again and arborizes in the gland in a rather regular way. The small arterial capillaries fall into the much wider sinusses. With regard to the veins in relation with this gland, none of my series is in such a condition that all details could be observed completely. At the caudal end of the gland a number of sinusses and vessels is situated in the reticular tissue, surrounding the spinal cord. More caudad these sinusses decrease in size and at the end of my series they have almost quite disappeared.

It was very evident that the blood is gathered from the gland in two veins situated at both sides of the gland immediately against its periphery. In the best series, in which the brain with the gland is prepared out of the cartilaginous skull and vertebrae this lateral vein is thickest in about the midst of the gland, also it has here a well developed wall. From this place the vein spreads as well in frontal as in caudal direction over the surface of the gland. The vein is cut off at place where it curves away from the gland in lateral direction, so I suppose that it leaves the vertebral canal here (fig. 6).

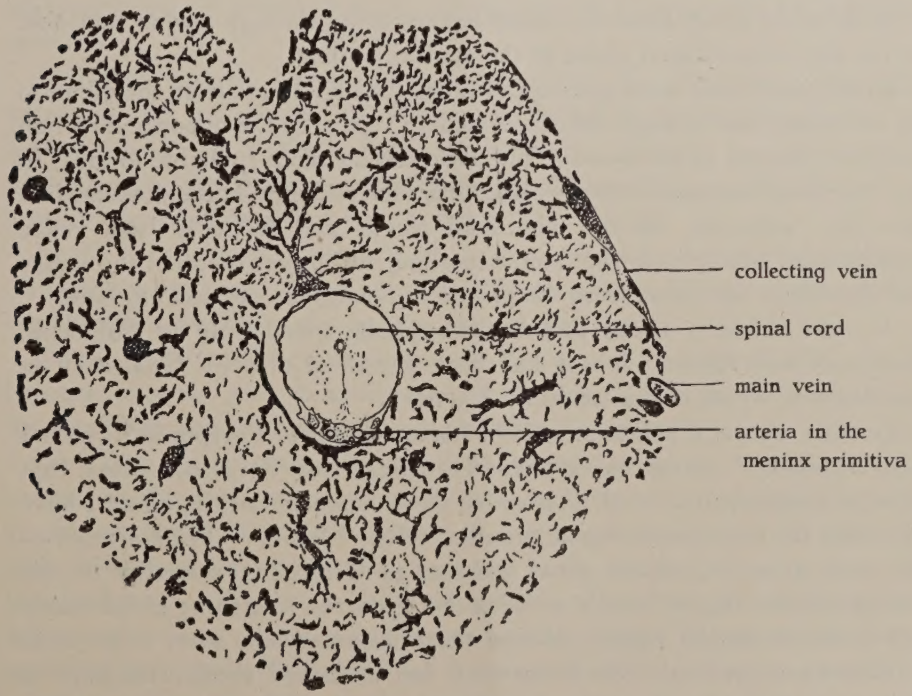

Fig. 6. Cross section showing the cervical cord surrounded by the myelencephalic gland of Polyodon. Only the bloodcavities of the gland are figured.

In another series a sheath of cartilage is left around the gland, but by the difference in contraction of the cartilage and the glandular tissue the sections are very much folded, some are even torn, so this series in general is less useful. However, I found here a vein leaving the vertebral canal together with a spinal nerve. At the frontal side a vessel strikes us, running at the dorsal side of the spinal cord from the gland to the choroid plexus of the fourth ventricle and splitting up in a number of sinusses lying on this menbrane (see also fig. 6). This vessel can be distinguished immediately from the other sinusses and veins by the great number of pigment cells lying along the thin wall in the same way as is the case in arteries.

Against the wall of other venous bloodvessels also pigment cells are found but in far smaller number.

Furthermore frontal of the gland and at the ventral side of the spinal cord a great number of venous cavities is found, which anastomose again and again. A little caudal of the calamus scriptorius a part of this cavities curves around the spinal cord in order to spread on the choroidal roof of the fourth ventricle.

Most of the blood, however, seems to flow away through a wide vein, that leaves the perimeningial tissue in the ventral midline.

It still remains an open question whether the blood runs from the gland to the choroidal roof through the dorso-median vein or in the opposite direction from the choroid to the gland. The latter seems more probable to me. In the first place because an artery comes from the midbrain in the dorsomedian line that arborises in the choroidal plexus and secundly both venae encephalicae posteriores, that run, according to STERZI, parallel the vagus and discharge the blood from the plexus in Selachians are lacking here.

As said before I found this myelencephalic gland only in Polyodon, Acipenser and Amia, while it has been described also by CHANDLER in Lepidosteus, which is confirmed by KAPPERS.

In other fishes, Cyclostomes, Selachians, Teleosts, Polypterus, which I have studied, I found no gland. However, this does not prove that there is really nothing at all. As one of the components of the gland I have described the very characteristic granular cells. I found — like KAPPERS — the same granular cells in great numbers in Ceratodus, scattered on the choroid plexus of the fourth ventricle between the numerous bloodvessels and in the meningial tissue. Indeed these granular cells seem to occur in vertebrates in general. So SUNDWALL has described them accurately in different mammals, they are mentioned also by DEWEY. GOLDMANN described them in rats as pyrrolcells. It is difficult to say in how far the mastcells, described by MCKIBBEN in Necturus, as also the "Wanderzellen" mentioned by KOLMER, correspond to the granulecells, as I found in Polyodon.

As said by MCKIBBEN, the mastcells in the meninges of Necturus, if studied superficially look like neurones on account of their long thin branches. Also the "Wanderzellen" figured by KOLMER in Triton have the same shape. It is remarkable that these cells occur also at the ventricular side of the choroid membrane. Although I do not doubt KOLMER's statement, I have never seen this in the preparations of the different amphibians, which I studied. According to KOLMER these cells occur in the choroid plexus of all vertebrates, so in the same place, where SUNDWALL and other authors found the more simply shaped granulecells. So it seems probable to me that we are dealing here with the same cells and that the difference in shape is only the result of the functional state and perhaps of the fixation. LEHNER also has shown that mastcells may make amoeboid movements and lately NEUMANN mentioned that also the eosinophil cells are able to do so.

I did not find the granule cells that occur in such a large number in the myelencephalic gland in the choroid of the fourth ventricle in Polyodon. This indicates that these cells, scattered in other vertebrates, are accumulated in a structure of definite form in these four fishes. This seems also to be the case in reptiles, but in a much less degree, at least KOLMER mentions accumulations of a typical shape on the choroid plexus near the calamus scriptorius.

Different authors have indicated (KAPPERS, KOLMER, a.o.) that the plexus can be vascularised to such an extent that it can be looked upon as a bloodgland. So KOLMER found all lymphatic elements in it in a great number especially in the dog and says that it gives the same impression as small pieces of bone marrow scattered on the choroid.

In the four mentioned ganoids we do not only find a localisation but also an enormous increase of the granule cells compared with other vertebrates. And furthermore the organ has the typical structure of a bloodgland.

There are different opinions about the function of the granule cells. Some authors suppose the granules to be nucleines, others derivatives of haemaglobine and the opinion exists also that the granules contain oxydases. I think that the granule cells are of phagocytic character. In the bloodcavities of the myelencephalic gland I found many more or less deformed erythrocytes and these were always in the neighbourhood of the granule cells. Also the granules are always stained in the same way as the nuclei of the erythrocytes. This was striking especially in the Weigert preparations, where only these granules and nuclei are intensively black, whereas the nuclei of the other cells are red by the contrastaining with paracarmin.

For an experimental research of the function of the granule cells, especially in relation to their situation on the choroid or in the neighbourhood of the brain, the fishes, mentioned in this article, are a very good material, because here the whole organ and together with this all granule cells can be removed easily, whereas in other vertebrates this is excluded on account of their widely spread occurrence.

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